Ozonization of Organic Substrates. Hydrotrioxide Formation and Decomposition to Give Singlet Oxygen[1]

Frank E. Stary, Dale E. Emge, and Robert W. Murray*

Contribution from the Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121. *Received July 7, 1975*

Abstract: Ozonization of benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether leads to intermediates which have been characterized as hydrotrioxides. The kinetics of the decomposition of these intermediates has been studied by NMR spectroscopy and decomposition activation energies determined. The decompositions give singlet oxygen which was characterized by its reactions with typical singlet oxygen acceptors.

Organic trioxides and tetroxides have received increasing attention in recent years. Evidence has been presented for the existence of members of both classes of compounds.[2-9] Organic hydrotrioxides are a class of compounds which are related to trioxides in the same manner as hydroperoxides are related to peroxides. Hydrotrioxides have been postulated to be intermediates in the ozonization of a variety of organic substrates. These substrates include hydrocarbons,[10-12] silanes,[13] ethers,[14,15] alcohols,[11] amines,[16-18] aldehydes,[19,20] and diazo compounds.[21] While in most of these cases hydrotrioxides appear to be reasonable structures for ozonization intermediates, little experimental evidence has been available to confirm their existence and recently arguments have been put forth[22] against their intermediacy in some hydrocarbon ozonizations. There is some evidence for the existence of the parent, nonorganic compound, hydrogen trioxide. This species has been postulated to be produced when water saturated with oxygen is irradiated with an intense electron beam[23] or when atomic hydrogen reacts with ozone at low temperature.[24] Experimental evidence concerning the existence, properties, stability, and chemistry of organic hydrotrioxides is sparse, however.

We have been studying the reactions of ozone with organic substrates as possible sources of singlet oxygen.[25-30] In a number of these cases, we have provided evidence that singlet oxygen is produced in the ozonization reaction, and in some cases such ozonizations are very convenient and efficient sources of singlet oxygen for chemical oxygenation reactions.

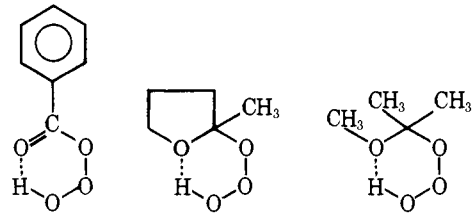
In one of these earlier cases, that of isopropyl ether,[30] we suggested that the ozonization intermediate was a hydrotrioxide which decomposed upon warming to give acetone, isopropyl alcohol, and singlet oxygen. This suggestion was based upon product analysis and a low-temperature NMR study which gave a spectrum which could be reasonably assigned to the hydrotrioxide structure.

In this paper we report further evidence for the formation of hydrotrioxides in certain ozonization reactions. We also describe the results of kinetic studies of the decomposition of the hydrotrioxides as well as present evidence that these decompositions produce singlet oxygen which can be used to oxygenate suitable singlet oxygen acceptors.

Results and Discussion

When neat benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether are ozonized at low temperature and the ozonized solutions then allowed to warm to room temperature, an exothermic reaction is observed to occur with vigorous evolution of a gas. These observations along with our earlier NMR observations in the case of diisopropyl ether[30] and the numerous suggestions that hydrotrioxides could be involved in these or similar ozonizations[10-21] prompted us to begin a careful low-temperature NMR study of these ozonizations in hopes of confirming the presence of the postulated hydrotrioxides. Erickson et al. had also noticed[14] the exothermic decomposition of an intermediate in the ozonization of diisopropyl ether and had concluded that the intermediate was the hydrotrioxide. Also White and Bailey had reported[19] the evolution of oxygen during the ozonization of benzaldehyde using ozone–nitrogen.

In each of the substrates, benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether, the low-temperature NMR spectrum contains an absorption at ca. δ 13.1 which is consistent with the expected large deshielding[31] in the intramolecularly hydrogen-bonded hydrotrioxides, **1–3,** respectively.



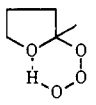
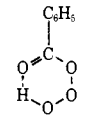
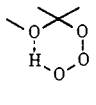
1 **2** **3**

Additional supportive evidence for the intramolecular hydrogen-bonded structures comes from the observation that the chemical shift of these absorptions shows little change with dilution. The small observed change, ca. 0.10 ppm, is consistent with that observed by Swern et al.[32] for peroxypelargonic acid (ca. 0.17 ppm) and is quite different than the change in shift which they observed (ca. 1.14 ppm) when pelargonic acid itself was diluted. These authors attributed the relative insensitivity to dilution of chemical shift in the peroxy acid to the presence of an intramolecular hydrogen-bonded structure.

The absorptions attributed to the hydrotrioxides, **1–3,** all were observed to decay by a first-order kinetics process. The rate of decay of the hydrotrioxide proton absorption could be conveniently followed by integrating the peak area with time. In all cases, plots of logarithms of integrated peak areas vs. time were linear over several half-lives. A summary of the results obtained in this manner is given in Table I.

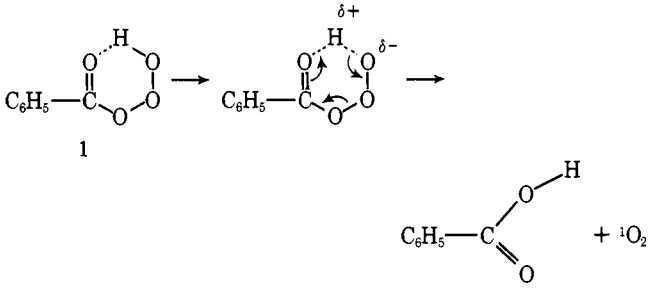
By using the NMR integration method at several temperatures, it was possible to obtain the activation energies for the decomposition of the presumed hydrotrioxides in the neat substrates in the cases of benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether. When these results indicated rather low A factors in the benzaldehyde and 2-methyltetrahydrofuran cases, it was decided to study the decompositions in diethyl ether solvent in addition to the neat substrates. The results of these experiments are summarized in Table II. As will be noted the activation

Table I. Summary of Kinetic Results for the Decomposition of Hydrotrioxides

Hydrotrioxide	Solvent	Temp, °C	Rate constants, k_1, s^{-1}
	2-MeTHF	−6	$3.68 \pm 0.33 \times 10^{-3}$
		−30	$6.88 \pm 0.28 \times 10^{-4}$
		−50	$2.06 \pm 0.06 \times 10^{-4}$
		−68	$3.45 \pm 0.35 \times 10^{-5}$
		−11.5	$1.50 \pm 0.03 \times 10^{-3}$
	2-MeTHF + Et_2O[a]	−12	$1.37 \pm 0.04 \times 10^{-3}$
		−18.5	$6.54 \pm 0.12 \times 10^{-4}$
		−26.5	$1.88 \pm 0.09 \times 10^{-4}$
		−32.5	$8.33 \pm 0.15 \times 10^{-5}$
	C_6H_5CHO	12	$1.67 \pm 0.23 \times 10^{-3}$
		0	$8.58 \pm 0.15 \times 10^{-4}$
		−8.5	$3.45 \pm 0.04 \times 10^{-4}$
		−20	$1.69 \pm 0.09 \times 10^{-4}$
		−34	$4.57 \pm 0.09 \times 10^{-5}$
	C_6H_5CHO + Et_2O[b]	−19	$8.90 \pm 0.60 \times 10^{-4}$
		−26.5	$2.82 \pm 0.06 \times 10^{-4}$
		−32.5	$1.41 \pm 0.03 \times 10^{-4}$
		−39	$5.29 \pm 0.26 \times 10^{-5}$
	—O—<	−9	$4.61 \pm 0.31 \times 10^{-3}$
		−10	$4.46 \pm 0.14 \times 10^{-3}$
		−22	$8.78 \pm 0.29 \times 10^{-4}$
		−25.5	$7.32 \pm 0.24 \times 10^{-4}$
		−33	$2.16 \pm 0.13 \times 10^{-4}$
		−37.5	$9.54 \pm 0.27 \times 10^{-5}$

[a] 2-MeTHF 15.4%, Et_2O 84.6% (by weight). [b] C_6H_5CHO 21.3%, Et_2O 78.7% (by weight).

energies are lower in the neat substrate decompositions. This is presumably due to the increased polarity of the neat solvents as compared to the diethyl ether solutions. A reasonable transition state for the decomposition proceeding from the six-membered intramolecularly hydrogen-bonded structures would involve development of charge separation along the reaction coordinate. In the case of benzaldehyde hydrotrioxide, for example, such a process would give benzoic acid and singlet oxygen. Such transition states should be stabilized by more polar solvents.



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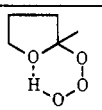
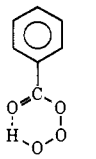
The effect of the solvent on the A factors is more difficult to explain. Development of charge separation along the reaction coordinate presumably would require considerable reorientation and ordering of solvent molecules associated with the hydrotrioxide.[33] This effect should be more pronounced in the polar neat solvents. This observation that E_a and log A are sensitive to solvent but change in a compensatory manner is similar to that reported[34] by Alder and Leffler for the decomposition of phenylazotriphenylmethane.

Further support for the hydrotrioxide structure for these ozonization intermediates comes from a comparison of the activation energies obtained (Table II) with those reported for several trioxides. Thus, Bartlett and Günther have reported[3] a $\Delta H^{\ddagger} \approx 23$ kcal/mol for the decomposition of di-*tert*-butyl trioxide. We earlier reported[28] that triphenyl phosphite ozonide, a cyclic trioxide, has an activation energy for decomposition of 14.1 ± 1.8 kcal/mol, a value which has been confirmed by Koch.[35] Also Benson and Shaw have estimated[36] an activation energy of 17.5 kcal/mol for the

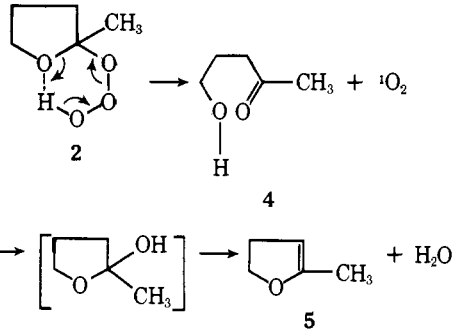
Table II. Summary of Activation Energy Data for Hydrotrioxides

Hydrotrioxide	Solvent	E_a, kcal/mol	Log A
	2-MeTHF	8.04 ± 0.2	4.1 ± 0.3
	2-MeTHF + Et_2O[a]	17.4 ± 0.4	11.7 ± 0.4
	C_6H_5CHO	10.7 ± 0.2	5.4 ± 0.4
	C_6H_5CHO + Et_2O[b]	16.4 ± 0.7	11.1 ± 0.6
	—O—<	16.6 ± 0.6	11.5 ± 0.5

[a] 2-MeTHF 15.4%, Et_2O 84.6% (by weight). [b] C_6H_5CHO 21.3%, Et_2O 78.7% (by weight).

decomposition of the cyclic trioxide (initial ozonide) obtained[37,38] from ozone and *trans*-1,2-di-*tert*-butylethylene. It is also pertinent that Whiting et al.[11] found that an intermediate produced in the ozonization of 2-propanol, which was assigned a hydrotrioxide structure, decomposed at a rate which was comparable to that reported for di-*tert*-butyl trioxide.[3]

In the cases of benzaldehyde and 2-methyltetrahydrofuran separate ozonizations were carried out for product analysis purposes so that products could be compared with those expected from decomposition pathways for the hydrotrioxides described above. After several attempts using a combination of distillation at reduced pressure and GLC analysis it was decided not to try and isolate directly the expected decomposition product, 5-hydroxy-2-pentanone (**4**), of 2-methyltetrahydrofuran hydrotrioxide. The distillation and GLC work indicated that the product was being formed but was undergoing further cyclization and dehydration reactions in the work-up. Thus, the GLC analysis of various distillation fractions showed the presence of water and a substance whose odor and infrared spectrum suggested that it was 2-methyl-4,5-dihydrofuran (**5**), the expected product of sequential cyclization and dehydration reactions of 5-hydroxy-2-pentanone. This conversion of **4** to **5** had been ob-



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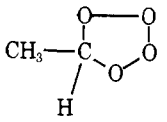
served previously by Schniepp et al.[39] In this case then, the product was ultimately identified as its semicarbazone and 2,4-dinitrophenylhydrazone. When carried out on a quantitative basis the 2,4-dinitrophenylhydrazone derivatization experiment indicated that the 5-hydroxy-2-pentanone product was formed in ca. 70% yield based on ozone absorbed. In the ozonization for product identification purposes the ozonized substrates were allowed to warm to room temperature after ozonization. Under these conditions vigorous gas evolution accompanying an exothermic reaction was evident. This evolution became evident at 12 and 10 °C for 2-methyltetrahydrofuran and benzaldehyde, respectively.

Because of the known[19,20,40,41] catalysis of autoxidation of benzaldehyde by ozone it was necessary to use an ozone–nitrogen[42-46] stream for the ozonizations for product study in this case. The expected product, benzoic acid, could be isolated in ca. 95% yield.

In the case of methyl isopropyl ether no attempt was made to isolate the products of decomposition of the hydrotrioxide. However, the NMR spectrum indicated the formation of acetone, the expected product of decomposition from a cyclic six-membered ring transition state.

The results obtained here confirm that the ozonization of benzaldehyde proceeds through the initial formation of a hydrotrioxide as postulated earlier by White and Bailey[19] and Erickson et al.[20] The report by White and Bailey also discusses several possible fates for the hydrotrioxide including the evolution of oxygen with concomitant formation of benzoic acid. Our work, particularly the singlet oxygen studies described below, suggests that this is probably the predominant reaction pathway for the hydrotrioxide. We cannot exclude a contribution from the reaction pathway involving homolysis of the hydrotrioxide and ultimate formation of perbenzoic acid as suggested by Bailey and White,[19] however. Presumably any perbenzoic acid formed in this manner in neat benzaldehyde would undergo a further reaction with the benzaldehyde to give 2 mol of benzoic acid.

It should also be noted that Syrov and Tsyskovskii, in discussing[47] the mechanism of ozonization of acetaldehyde, have considered the possibility that a cyclic tetroxide, **6**



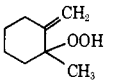
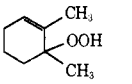
6

could be formed. These authors further postulate that if **6** is formed, it should be unstable and would rapidly rearrange to the hydrotrioxide. It seems unlikely that structures corresponding to **6** are responsible for the NMR absorptions which we have assigned to the hydrotrioxides. The cyclic tetroxide methine proton absorption should have approximately the same chemical shift (ca. δ 5.0) as that observed for ring methine protons in ozonides.[48]

An additional observation was made during the course of the NMR kinetic studies which requires comment. In the case of 2-methyltetrahydrofuran the hydrotrioxide proton NMR absorption consisted of two peaks centered at δ 13.08 with the downfield peak being slightly less intense. Furthermore, the two peaks broadened as the temperature was raised until they finally merged to a broad singlet. This latter observation could suggest that a kinetic process, in addition to decomposition, was taking place. While the origin of the two peaks remains uncertain, it is possible that they are due to the presence of both cis and trans ring fusions in the six-membered intramolecularly hydrogen-bonded structure of the hydrotrioxide, **2**. If this were the correct explanation then the possible additional kinetic process could be the interconversion of these two forms.

Singlet Oxygen Studies. As indicated above our initial reason for studying the ozonizations described here was to determine whether or not such ozonizations produce intermediates capable of giving off singlet oxygen. When carrying out the ozonizations for this purpose the procedure followed was to ozonize the neat substrate at ca. −50 °C. Excess ozone was then purged out using a nitrogen stream. A calibrated ozone–oxygen stream along with two potassium iodide traps in series with the reaction vessel were used to determine the amount of ozone absorbed. A good singlet oxygen acceptor, 1,3-diphenylisobenzofuran, was then added to each of the ozonized substrates and they were allowed to warm to room temperature slowly. It was usually necessary to add a small amount of methylene chloride or acetone to maintain the acceptor in solution at the low temperature used. The room temperature reaction mixtures were then concentrated in vacuo and the wet crystals of the singlet oxygen product, *o*-dibenzoylbenzene, were recrystallized from dry benzene. Yields of the singlet oxygen product were 96, 80, and 30% from ozonized benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether, respectively. These results coupled with the NMR observations described above indicated that each of these substrates was ozonized to a hydrotrioxide intermediate and that these intermediates serve as useful sources of singlet oxygen with the singlet oxygen being evolved in the vicinity of 10 °C.

Table III. Product Distributions in the Oxidation of 1,2-Dimethylcyclohexene

		Method		
			Hydrotrioxide decomposition	
Product	$OCl^- - H_2O_2$	Photooxidn	PhCHO	2-MeTHF
	91[a]	89[a]	90[b]	92[b]
	9[a]	11[a]	10[b]	8[b]

[a] Reference 49. [b] This work.

In order to obtain further evidence that the oxidant was indeed singlet oxygen, we used the technique of Foote et al.[49] in which an acceptor is added which can give more than one single oxygen product. Product distribution can then be compared with that obtained under known singlet oxygen conditions. In these experiments the procedure was similar to that described above except that the ozonizations were carried out at −23 °C and only benzaldehyde and 2-methyltetrahydrofuran were used. The singlet oxygen acceptor used, 1,2-dimethylcyclohexene, was added at the low temperature and the reaction mixtures were allowed to warm to room temperature. The expected hydroperoxide products were then reduced to the corresponding alcohols by $NaBH_4$ prior to GLC analysis. The results of these experiments (Table III) indicate that for both ozonized benzaldehyde and 2-methyltetrahydrofuran the expected singlet oxygen products are produced in essentially the same distribution as given by sensitized photooxidation or by using the hypochlorite–hydrogen peroxide[49] method for producing singlet oxygen.

Experimental Section

Materials. 2-Methyltetrahydrofuran was purified by fractional distillation on a Nester-Faust NFT-51 adiabatic annular spinning band column. Reagent grade benzaldehyde was purified by the method of Vogel.[50]

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Ozonizations. Ozone was produced in a Welsbach Model T-408 ozonator operated to deliver ca. 0.25 mmol of ozone per minute in the sample stream.

Ozonizations of the neat substrates were carried out at −23 °C in a Dewar flask containing a CCl_4–liquid N_2 slush, unless otherwise indicated. Total ozonization time was 15 min. Immediately after ozonization the reaction mixtures were transferred to a series of NMR tubes and decomposition of reaction products was slowed by immersing these tubes in liquid nitrogen. The tubes were then

transferred to a dry ice-acetone bath just before kinetic studies were begun. In those cases where solvents other than the neat substrates were used, the ozonized substrates were diluted to the specified solvent compositions (Table I) prior to storage in the liquid nitrogen bath.

Kinetic Studies. A. 2-Methyltetrahydrofuran Hydrotrioxide. The NMR tubes containing the ozonized 2-methyltetrahydrofuran were inserted into the probe of a Perkin-Elmer R-20 NMR spectrometer which was precooled to the desired temperature for each of the temperatures used (Table I). The hydrotrioxide signal consisted of two peaks centered at δ 13.08[51] at −50 °C. Line widths at half height were 0.3 ppm at −54 °C, 1.0 ppm at −30 °C, and 2.0 ppm at −27 °C. The center of the signals shifted ca. 0.1 ppm upfield upon warming the sample from −60 °C to −30 °C. As the temperature was raised broadening of the two peaks was sufficient to cause them to merge to a broad singlet at −27 °C.

The first-order decay of the hydrotrioxide proton signal was followed by integrating the peak area with time at a number of temperatures (Table I). The plots of the logarithm of integrated peak areas vs. time were linear over several half-lives. At least five points were used in determining each rate constant. The rate constants and activation energy were determined using a Wang 700 series advanced programming calculator and a least-squares program to process the experimental data. The errors were determined from the scatter of the experimental data using the method of Whittaker and Robinson.[52] An Arrhenius plot gave E_a = 8.04 ± 0.2 kcal/mol and log A = 4.1 ± 0.3 for decomposition of the hydrotrioxide in neat 2-methyltetrahydrofuran. When a similar procedure was followed using diethyl ether to dilute the 2-methyltetrahydrofuran then E_a was found to be 17.4 ± 0.4 kcal/mol and log A = 11.7 ± 0.4.

B. Benzaldehyde Hydrotrioxide. A similar procedure to that described above for the 2-methyltetrahydrofuran case was followed. The ozonized benzaldehyde shows an absorption at δ 13.1 at −50 °C which is assigned to the hydrotrioxide. This absorption shifts upfield by ca. 0.2 ppm as the reaction mixture is warmed to −20 °C. The line width at half height was ca. 0.1 ppm at −50 °C and ca. 0.4 ppm at −20 °C. This absorption decayed by a first-order process. The absorption was integrated and the data treated as described above. An Arrhenius plot gave E_a = 10.7 ± 0.2 kcal/mol and log A = 5.4 ± 0.4. When the decomposition occurs in a mixed benzaldehyde-diethyl ether solution (Table I) then E_a = 16.4 ± 0.7 kcal/mol and log A = 11.1 ± 0.6.

C. 2-Hydrotrioxy-2-methoxypropane (Methyl Isopropyl Ether Hydrotrioxide). A similar kinetic analysis was conducted on the samples of ozonized methyl isopropyl ether. In this case the hydrotrioxy proton absorption occurs at δ 13.21. An Arrhenius plot gives E_a = 16.6 ± 0.6 kcal/mol and log A = 11.5 ± 0.5 for decomposition of the hydrotrioxide in neat methyl isopropyl ether.

Ozonizations. Product Studies. A. 2-Methyltetrahydrofuran. Ozonization was carried out as described above except that the ozonized 2-methyltetrahydrofuran was allowed to warm to room temperature and fractional distillation using a Nester-Faust spinning band column attempted on the crude reaction mixture. Under these conditions vigorous gas evolution, accompanied by a sharp temperature rise in the reaction mixture, is evident beginning at ca. 12 °C. After several attempts at various reduced pressures it became apparent that the expected product, 5-hydroxy-2-pentanone, was decomposing under the distillation conditions. When GLC analysis was used to examine some of the distillation fractions obtained it was found that they contained varying amounts of unreacted 2-methyltetrahydrofuran, water, 5-hydroxy-2-pentanone, and a material which had a characteristic olefinic odor and infrared absorption indicating a carbon-carbon double bond. Apparently the product 5-hydroxy-2-pentanone was cyclizing and dehydrating to give 2-methyl-4,5-dihydrofuran.[39]

In separate experiments the room temperature reaction mixture was treated with semicarbazide and 2,4-dinitrophenylhydrazine to give 5-hydroxy-2-pentanone semicarbazone, mp 154.2-156.4 °C (lit.[53] mp 154-155 °C), and 5-hydroxy-2-pentanone 2,4-dinitrophenylhydrazone, mp 147.3-149.0 °C (lit.[54] mp 150 °C), respectively. When the experiment with 2,4-dinitrophenylhydrazine was carried out on a quantitative basis it was found that an absorption of 3.6 mmol of ozone by the 2-methyltetrahydrofuran led to the production of 0.71 g (2.51 mmol, 70%) of 5-hydroxy-2-pentanone 2,4-dinitrophenylhydrazone.

B. Benzaldehyde. In order to minimize the known autoxidation of benzaldehyde to benzoic acid, ozonization for product study in this case was carried out by using ozone in a nitrogen rather than an oxygen stream. The ozone from the generator was absorbed onto a precooled silica gel column according to the procedure of Reimschuessel and Mountford.[42] The ozone was then desorbed with nitrogen as required. Ozonization was carried out as above except for use of nitrogen instead of oxygen as carrier gas and the reaction mixture allowed to warm to room temperature. Gas evolution was evident beginning at ca. 10 °C. At room temperature the reaction mixture was clear and had a pale yellow color. Excess benzaldehyde was removed in vacuo to give oily yellow crystals. The crystalline residue was then sublimed to give white crystals of benzoic acid, mp 120.5-121 °C (lit.[55] mp 122.4 °C). When this experiment is carried out on neat benzaldehyde which has absorbed 0.904 mmol of ozone then the yield of benzoic acid is 0.107 g (0.87 mmol, 96%). If the hydrotrioxide decomposition is followed by NMR as described above then the absorption at δ 11.5 due to the acid proton of benzoic acid can be observed to appear as the hydrotrioxide proton absorption at δ 13.1 disappears.[56]

Singlet Oxygen Studies. A. Benzaldehyde. Neat benzaldehyde was ozonized at −50 °C using the O_3-O_2 stream. After ozonization the reaction mixture was purged with N_2 to remove excess ozone. At this point 1.1 mol of ozone had been absorbed. 1,3-Diphenylisobenzofuran (2.2 mol) was added to the cold reaction mixture. Methylene chloride (ca. 2 ml) was then added to help keep the 1,3-diphenylisobenzofuran in solution. The reaction mixture was then allowed to warm to room temperature slowly. The excess benzaldehyde was removed in vacuo and the wet solid obtained was recrystallized from dry benzene[57] to give white crystals of *o*-dibenzoylbenzene, mp 144.7-146 °C (lit.[58] mp 146-147 °C). Yield was 96%.

In a separate experiment 50 mmol of benzaldehyde was ozonized at −23 °C until 1.0 mmol of O_3 was absorbed. The reaction mixture was then flushed with N_2 to remove excess ozone and 0.8 ml (6.08 mmol) of 1,2-dimethylcyclohexene was added. The reaction mixture was swirled to give a homogeneous solution and then removed from the cooling bath and allowed to warm to room temperature. After standing at room temperature for 1.0 h the reaction mixture was cooled in an ice bath and 0.5 g (13.2 mmol) of $NaBH_4$ added. Water (ca. 3 ml) was then slowly added to give two phases. The reaction mixture was then stirred overnight with a magnetic stirrer. The aqueous layer was separated off and the organic layer analyzed by preparative GLC using a 4-ft FFAP column at 105 °C. Yields and distribution of the alcohol products were determined using an Autolab Model 6300 digital integrator. The alcohol products, 1-methyl-2-methylenecyclohexanol and 1,2-dimethylcyclohex-2-en-1-ol, were identified from their infrared and NMR spectra. Yields (based on O_3 absorbed) were 51.3 and 5.8%, respectively.

B. 2-Methyltetrahydrofuran. The substrate (5.0 ml) was ozonized at −70 °C for 15 min. The reaction mixture was then flushed with N_2 to remove excess ozone. Total ozone absorbed was 3.64 mmol. The acceptor, 1,3-diphenylisobenzofuran (7.28 mmol, 2:1 excess) was added to the cold reaction mixture. Acetone (ca. 2 ml) was added to ensure solution of the acceptor. The reaction mixture was then allowed to slowly warm to room temperature. The excess 2-methyltetrahydrofuran was removed in vacuo and the solid obtained was recrystallized from dry benzene to give white crystals of *o*-dibenzoylbenzene, mp 144-148 °C (lit.[58] mp 146-147 °C), mmp 144-148 °C. Yield was 80.1%.

In a separate experiment the 2-methyltetrahydrofuran was ozonized at −23 °C and the ozonized substrate treated with the acceptor 1,2-dimethylcyclohexene in the same manner as described above for the benzaldehyde case. In the 2-methyltetrahydrofuran case yields of 1-methyl-2-methylenecyclohexanol and 1,2-dimethylcyclohex-2-en-1-ol were 39.7 and 3.5%, respectively.

C. Methyl Isopropyl Ether. The neat substrate was ozonized at −23 °C for 15 min. The reaction mixture was then flushed with N_2 to remove excess ozone. Total ozone absorbed was 2.33 mmol. The acceptor, 1,3-diphenylisobenzofuran (0.33 g, 1.22 mmol) was added to the cold reaction mixture. The reaction mixture was then allowed to slowly warm to room temperature. The excess substrate was removed in vacuo and the solid obtained was recrystallized from dry benzene to give white crystals of *o*-dibenzoylbenzene, mp 142-144 °C (lit.[58] mp 146-147 °C; yield was 0.201 g (30%).

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Oxidation of Primary Amines Bound to Bis(2,2′-bipyridine)ruthenium(II)

F. Richard Keene, Dennis J. Salmon, and Thomas J. Meyer*

Contribution from the W. R. Kenan, Jr., Laboratories of Chemistry, Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. *Received July 12, 1975*

Abstract: In the net sense, chemical and electrochemical oxidations of the ions $[Ru(bpy)_2(NH_2CH_2R)_2]^{2+}$ (NH_2CH_2R = allylamine, benzylamine, and *n*-butylamine) occur by dehydrogenation at the amine ligands giving the corresponding bis(nitrile) complexes, $[Ru(bpy)_2(N{\equiv}CR)_2]^{2+}$. The reactions appear to proceed by initial oxidation of Ru(II) to Ru(III), followed by a series of stepwise dehydrogenation reactions which occur via imine intermediates.

Net reactions involving the oxidative dehydrogenation of chelated amines to imines have been reported for macrocyclic amines,[1,2] and for ethylenediamine and related diamines.[3-7] For chelated amines, dehydrogenation stops at the imine stage; further oxidation gives hydroxodiimines[8] or net decomposition, rather than nitriles.[7]

There are two examples of the oxidation of monodentate primary amines to nitriles or cyanides. McWhinnie et al.[9] have reported the isolation of Ru(III) products containing the cyanide ion following the aerial oxidation of $[Ru(NH_2CH_3)_6]^{2+}$, and Diamond, Tom, and Taube[10] have shown that benzylamine bound to pentaammineruthenium(II) can be oxidized to benzonitrile.

Previous work has shown that oxidation of ligands bound to bis(2,2′-bipyridine)ruthenium(II) can be facile, and quantitative.[7,11] The reactions appear to proceed via initial oxidation of Ru(II) to Ru(III), followed by a series of rapid steps in which the net reactions involve the oxidation of a coordinated ligand.

Experimental Section

Electronic spectra were recorded on a Bausch and Lomb 210UV spectrophotometer. ^1H NMR spectra were measured on a Jeol C-60-HL spectrometer using acetone-d_6 solutions of PF_6^- salts