

rence for retro-Diels-Alder reaction yielding *cis*-azomethane is a result of decreased "through space," n, π interaction of **3** compared to **1**. Hoffmann, Heilbronner, and Gleiter¹² have pointed out that whereas the dominant π, π interaction of norbornadiene is "through space," that of 1,4-cyclohexadiene is "through bond." By analogy, then, the n, π "through space" interaction of **1** is expected to be larger than that of **3**. The presence of a substantial n, π interaction in **1** is indicated by its surprisingly long wavelength uv absorption.⁷

We are continuing our studies in this area, attempting to measure the difference in activation parameters for decomposition of syn and anti bicyclic compounds and to define the utility of the method for stereoselective preparation of *cis* azo compounds.

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Hydrotrioxides. Formation and Kinetics of Decomposition

Sir:

Hydrotrioxides have been suggested as intermediates in the ozonization of a variety of organic substrates including hydrocarbons,¹⁻³ silanes,⁴ ethers,^{5,6} alcohols,² amines,⁷⁻⁹ aldehydes,¹⁰ and diazo compounds.¹¹ Little experimental evidence has been available concerning the possible existence of hydrotrioxides, and, recently, arguments have been put forth¹² against their intermediacy in some hydrocarbon ozonizations.

We have been studying the reaction of ozone with organic substrates as possible sources of singlet oxygen.¹³⁻¹⁸ In one of these cases, isopropyl ether, we

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suggested that the product of ozonization was a hydrotrioxide which decomposed to give singlet oxygen, acetone, and isopropyl alcohol. This conclusion was based on product analysis and on a low temperature nmr study¹⁸ which gave a spectrum which could reasonably be assigned to the hydrotrioxide structure.

There is some evidence for the existence of the parent compound, hydrogen trioxide. This species has been postulated to be produced when water saturated with oxygen is irradiated with an intense electron beam¹⁹ or when atomic hydrogen reacts with ozone at low temperature.²⁰ There is little known about the properties, stability, and chemistry of organic hydrotrioxides, however.

We report here additional evidence for the formation of hydrotrioxides upon ozonization of organic substrates, as well as results of kinetic studies of their decomposition.

In our continuing search for sources of singlet oxygen in ozone chemistry, we have ozonized benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether at low temperatures. The low temperature nmr spectrum of each of these ozonized substrates contains an absorption which we feel is consistent with the presence of the hydrotrioxide structure. These absorptions uniformly occur at *ca.* δ 13.1 consistent with the expected large deshielding²¹ in an intramolecularly hydrogen-bonded hydrotrioxide. The absorptions decay following first-order kinetics. The rate of decay of the hydrotrioxy proton absorption can be conveniently followed by nmr, and, by using this procedure at several temperatures, the activation energies for the decomposition of the presumed hydrotrioxides have been determined.²² It should also be noted that the position of the hydrotrioxide proton shows little change in chemical shift with the dilution accompanying decomposition. The observed change in chemical shift with dilution, *ca.* 0.10 ppm, is consistent with that observed by Swern, *et al.*,²³ for peroxy-pelargonic acid (*ca.* 0.17 ppm) and quite different than the change in shift which they observed (*ca.* 1.14 ppm) when pelargonic acid itself was diluted. These latter authors attribute the relative insensitivity to dilution of chemical shift in the peroxy acid to the intramolecular hydrogen-bonded structure of the peroxy acid. Application of a similar argument here lends support to the proposed intramolecularly hydrogen-bonded hydrotrioxide structure.

In a typical experiment, benzaldehyde was ozonized,²⁴ either neat or in diethyl ether solution, for 15 min at -23° in a Dewar flask containing a CCl_4 slush. The ozonized solution was then transferred to a series of nmr tubes which were stored at liquid nitrogen temperature until the time the spectra were recorded. At -50° the spectrum contained an absorption at δ 13.04 which is assigned to the hydrotrioxide proton.

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
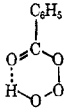


(22) In all cases singlet oxygen was found to be a product of the decomposition of the presumed hydrotrioxide. Details of these experiments will be given in the full paper.

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(24) Ozone was provided by a Welsbach Corp. Model T-408 ozonator operated to give a sample stream containing *ca.* 0.25 mmol of O_3/min .

Integration of this absorption with time indicated a first-order decomposition process. A summary of the kinetic data for benzaldehyde hydrotrioxide and the other cases studied is given in Table I. The tempera-

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

Hydrotrioxide	Solvent	Temp, °C	Rate constant, k_1 , sec ⁻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	$(1.50 \pm 0.03) \times 10^{-3}$
	C ₆ H ₅ CHO	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 ₆ H ₅ CHO + Et ₂ O ^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	$(5.29 \pm 0.26) \times 10^{-5}$
		-9	$(4.61 \pm 0.31) \times 10^{-3}$
	-O-<	-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%; Et₂O, 84.6% (by wt). ^b C₆H₅CHO, 21.3%; Et₂O, 78.7% (by wt).

ture variation of the rate of decomposition of benzaldehyde hydrotrioxide in diethyl ether solvent permitted a calculation of E_a (16.4 ± 0.7 kcal/mol) and $\log A$ (11.1 ± 0.6).²⁵

Similar experiments were carried out on 2-methyltetrahydrofuran and methyl isopropyl ether. The kinetic data (Table I) indicate an $E_a = 17.4 \pm 0.4$ kcal/mol and $\log A = 11.7 \pm 0.4$ for 2-methyl-2-hydrotrioxytetrahydrofuran decomposition in diethyl ether solution and $E_a = 16.6 \pm 0.6$ kcal/mol and $\log A = 11.5 \pm 0.5$ for 2-hydrotrioxy-2-methoxypropane (methyl isopropyl ether hydrotrioxide) in neat methyl isopropyl ether. In the case of methyl isopropyl ether the hydrotrioxide proton absorbs at δ 13.21 and in the case of 2-methyltetrahydrofuran the hydrotrioxide proton absorption consists of two peaks centered at δ 13.08.²⁷

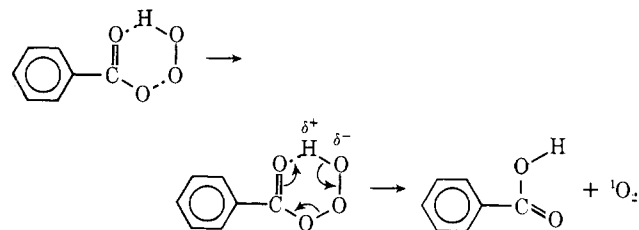
When the hydrotrioxides of benzaldehyde and 2-methyltetrahydrofuran are permitted to decompose in the neat substrates (Table I) then the kinetic analysis leads to $E_a = 10.7 \pm 0.2$ kcal/mol and $\log A = 5.4 \pm 0.4$ and $E_a = 8.04 \pm 0.2$ kcal/mol and $\log A = 4.1 \pm 0.3$ for benzaldehyde and 2-methyltetrahydrofuran

(25) In all cases error analysis was carried out by computer using the method of Whittaker and Robinson.²⁶ Plots of integrated peak area vs. time were linear over several half-lives.

(26) E. Whittaker and G. Robinson, "The Calculus of Observation," 4th ed, Blackie and Sons, Limited, London, 1958, Chapter IX.

(27) While the origin of the two peaks in this case is not known for certain, a possibility is the presence of both cis and trans ring fusions in the six-membered intramolecularly hydrogen-bonded structure of the hydrotrioxide.

hydrotrioxides, respectively. This lowering of the activation energies in the cases of the hydrotrioxides of benzaldehyde and 2-methyltetrahydrofuran 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 toward, for example, benzoic acid and singlet oxygen, in the case of benzaldehyde hydrotrioxide. Such a transition state should be stabilized by more polar solvents.



The effect of solvent on the A factors is more difficult to explain, but presumably, arises from a reorientation of solvent molecules around the hydrotrioxide as it proceeds along the reaction coordinate toward the more polarized transition state.²⁸

The observation that E_a and $\log A$ are sensitive to solvent but change in a compensating manner is similar to that reported²⁹ by Alder and Leffler for the decomposition of phenylazotriphenylmethane.

A comparison of the activation energies from decomposition of the presumed hydrotrioxides reported here with those reported for several trioxides lends support to the assignment of the hydrotrioxide structures. Bartlett and Günther have reported³⁰ a $\Delta H \approx 23$ kcal/mol for the decomposition of di-*tert*-butyl trioxide. Benson and Shaw have estimated³¹ an activation energy of 17.5 kcal/mol for the decomposition of the cyclic trioxide (initial ozonide) obtained^{32,33} from ozone and *trans*-1,2-di-*tert*-butylethylene. Also, we have reported³⁴ that triphenyl phosphite ozonide, another cyclic trioxide, has an activation energy for decomposition of 14.1 ± 1.8 kcal/mol, a value which has been confirmed by Koch.³⁵

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