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THE OZONOLYSIS OF ORGANOMERCURIALS

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Since little has been reported about the reaction of organometallics with ozone,[1] and practically nothing about the specific reaction of organomercurials with the reagent,[2] we feel the necessity to communicate our initial results in the latter area.

Over ten different organomercurials have been ozonized in methylene chloride. A Welsbach T-408 ozonator was used to generate O_3 at the rate of 18 millimoles per hour,[3] and at a 2-4% concentration in oxygen. Nitrogen was used as the carrier gas in one run. The reaction temperatures were varied between -76, 0, and 10°C.

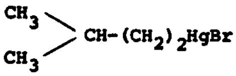
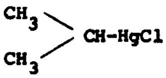
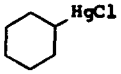
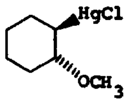
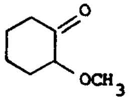
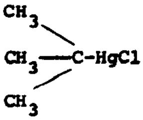
Identification and quantification of the organic products was performed by gas chromatographic analyses of the raw product mixtures. An inert, internal standard accompanied each ozonation to insure accurate G. C. results.

Amounts of ozone used in these reactions were calculated by knowing the O_3 flow rate and measuring the amount of liberated iodine in the KI trap after reaction.[3] Generally the reactions were run until there was no more absorbtion of ozone as detected by the above method. Reaction times varied between one and three hours, depending on the amount of mercurial,[4] the specific mercurial involved,[5] and the temperature of the reaction.[6]

In all reactions a solid immediately precipitated from the methylene chloride solution after the first introduction of ozone. These solids were separated during the work-up procedure, washed repeatedly with methylene chloride, dried, and analyzed by powder X-ray diffraction spectroscopy. The solids proved to be various inorganic salts of mercury I and II.[7]

The results of our studies to date are summarized in Table 1.

Table 1

	Organomercurial[4]	Carrier Gas	Reaction Temp.	Product[8]	Yield[8]
1.	$CH_3(CH_2)_5HgBr$	O_2	10°C.	Hexanoic acid Pentanoic acid Butanoic acid Propanoic acid Acetic acid Formic acid	30% 40% 10% 10% 5% ---
2.	$CH_3(CH_2)_5HgBr$	N_2[9]	10°C.	same as above[9]	same as above[9]
3.	$[CH_3(CH_2)_5]_2Hg$	O_2	10°C.	Hexanoic acid Pentanoic acid smaller acids	50% 20% 8-10% each
4.	$[CH_3(CH_2)_5]_2Hg$	O_2	-76°C.[6]	Hexanoic acid Pentanoic acid smaller acids	80% 5% ≤ 5% each
5.	$CH_3(CH_2)_2HgBr$	O_2	10°C.	Propanoic acid Acetic acid Formic acid	30% 35% 35%
6.	$[CH_3(CH_2)_2]_2Hg$	O_2	-76°C.[6]	Propanoic acid Acetic acid Formic acid	70% 15% 15%
7.	 $(CH_3)_2CH-(CH_2)_2HgBr$	O_2	0°C.	complex mixture[10]	---
8.	 $(CH_3)_2CH-HgCl$	O_2	10°C.	Acetone[11]	75%
9.		O_2	10°C.	Cyclohexanone[11]	60%
10.		O_2	0°C		---[12]
11.	 $(CH_3)_3C-HgCl$	O_2	10°C.	t-Butanol Acetone Formic acid	50% 22% 28%

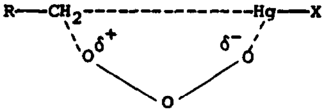
Scrutiny of Table 1 allows some generalizations. n-Alkylmercuric halides react with ozone to produce all possible acids upon chain breakdown. The di-n-alkyl analogs of these mercurials produce more of the parent carbon skeleton acid, and, at lower reaction temperatures, give even a greater yield of this product.

s-Alkylmercuric halides give fairly high yields of the ketone having the same parent carbon skeleton. t-Alkylmercuric halides, on the other hand, give substantial amounts of an alcohol with the parent carbon skeleton retained. However, as in the case of the n-alkylmercurials, cleavage of carbon-carbon bonds competes with formation of the main product.

The actual amount of ozone necessary to effect the above conversions varies somewhat but appears to lie between one and three moles for the tertiary and primary mercurials, respectively.[13] Moreover all attempts at isolating organic products of an intermediate oxidation state have failed, suggesting that cleavage of the carbon-mercury bond is the slow step of the reaction.[14]

Consideration of a possible mechanism for the ozonolysis of organomercurials should probably await further studies in this area. However, in view of the electrophilicity of ozone,[15] and the proposed mechanisms for electrophillic cleavage of carbon-mercury bonds,[16] a likely transition state for the first step might appear as in Figure 1.[17]

<u>Figure 1</u>



This transition state could then lead to the intermediate pictured in Figure 2.[17]

<u>Figure 2</u>

$$[R\text{—}CH_2\text{—}O\text{—}O\text{—}O\text{—}HgX]$$

The breakdown of this high energy species (Figure 2) could then take place <u>via</u> homolytic cleavage, although a heterolytic process might also be possible.

Our investigation now involves a complete rate study of this reaction. Hopefully the nature of the alkyl group as well as the mercury ligand will be related to the ease of carbon-mercury cleavage.[5] Attempts are also being made to prepare an organomercurial whose configuration will allow the determination of the reaction stereochemistry.

Finally, we are also exploring the synthetic utility of this reaction. Conversion of alkenes to various oxidation products <u>via</u> mercuration and ozonolysis (see reaction 10, Table 1) is being attempted in our laboratory.

Notes

1. Some work has been done on organotin, organolead, and organoselenium compounds. See the following, respectively: Yu. A. Aleksandrov, N. G. Sheyanov, and V. A. Shushunov, *C.A.*, **69**, 77388q (1968); B. V. Emel'yanov, Z. N. Shemyakina, and V. N. Shvarov, *C.A.*, **69**, 79964y (1968); G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962), and R. Pastyold and G. Bochmann, *C.A.*, **70**, 3190t (1969).

2. W. Bockemuller and L. Pfeuffer, *Ann.*, **537**, 178 (1939). Although the paper is entitled "Induced Peroxide Formation in the Bromination of Olefins," three sentences in the experimental section state that ozonolysis of diisopropyl mercury yielded acetone. Curiously no mention of the reaction was made throughout the rest of this or any other paper.

3. Rate of ozone output was calculated by the standard iodide-thiosulfate method.

4. Reactions were generally run on 10 to 20 millimoles (3-5 grams) of the organomercurial. The alkylmercuric halides were prepared from the Grignard reagents. See F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 145 (1960). The halides were in turn converted to the dialkylmercurial by the reaction of excess Grignard reagent.

5. Qualitative rate results in our laboratory show that $R_2Hg > RHgBr > RHgCl$, *i.e.*, follow the order for other electrophilic cleavages of organomercurials (see ref. 16, p. 4).

6. At -76°C. the reaction rate appeared greatly retarded.

7. In a typical ozonation of an alkylmercuric chloride, mercurous chloride, mercuric chloride, and mercuric oxide were identified as the inorganic byproducts. Efforts are now being made to assign specific yield percentages to these various compounds. Their stability towards excess ozone is also being studied.

8. Products whose yields were under 5% were not identified. Yields in most cases were by G. C. analysis and not isolated. Values are accurate to within ± 5%.

9. The silica gel method was used in this run. See P. S. Bailey and A. M. Reader, *Chem. Ind. (London)*, 1063 (1961). The fact that product ratios were not altered in the absence of oxygen does not preclude oxygen taking part in the reaction. A correlation with rate data might be of assistance in this matter.

10. N.M.R. showed that the products of this reaction were not only the expected acids, but also the tertiary hydrogen cleavage products.

11. No attempt was made to identify possible products of lower volatility.

12. Although this yield was not calculated, I.R. and N.M.R. showed no large amount of impurities in the raw product mixture. A 2,4-DNP derivative was used as final identification. See H. Adkins and A. G. Rossow, *J. Am. Chem. Soc.*, **71**, 3836 (1949) and D. D. E. Newman and L. N. Owen, *J. Chem. Soc.*, 4713 (1952).

13. It appears that cleavage of the carbon-mercury bond is not instantaneous. In the average reaction it was necessary to bubble seven to nine equivalents of O_3 through the reaction flask in order that two or three equivalents might react.

14. Partial ozonation produced only starting mercurial and final products.

15. J. S. Belew in R. L. Augustine, *Oxidation Vol. 1*; pp. 262-272. Marcel Dekker, Inc., New York (1969) and references cited therein.

16. F. R. Jensen and B. Rickborn, *Electrophilic Substitution of Organomercurials*; pp. 92-97. McGraw Hill, Inc., New York (1968) and references cited therein.

17. This type of transition state and intermediate has been proposed for other kinds of ozone cleavage reactions. See, for example, R. J. Ouellette and D. L. Marks, *J. Organometal. Chem.*, **11**, 407 (1968).