8.64 (m), 8.95 (m), 9.30 (s), 9.70 (s), 10.95 (m), 11.80 (w), and 14.35 μ (vs). Its mass spectrum showed no major peaks below 550. Molecular weight by osmometry was 761.

A similar chromatography on a mixture that came off the initial column after II but before the red material gave a colorless solid after crystallization from methanol. It melted at 80–94°. Its infrared spectrum showed peaks at 3.28 (s), 6.23 (s), 6.69 (s), 6.91 (s), 8.49 (w), 8.64 (m), 9.30 (s), 9.70 (s), 9.95 (w), 10.90 (w), 11.25 (s) 11.65 (m), 12.75 (s), 13.10 (vs), and 14.30 μ (vs). Its molecular weight by osmometric techniques was 1060.

A third hydrocarbon melting at 215–221° had infrared bands at 3.28 (s), 6.23 (s), 6.69 (s), 6.91 (s), 7.10 (m), 8.64 (m), 9.30 (s), 9.70 (s), 10.20 (w), 10.90 (m), 11.20 (m), 11.80 (w), 12.55 (m), 12.65 (m), 13.25 (vs), 13.80 (s), and 14.35 (vs). Molecular weight by osmometry was 441. (*Anal.* Found: C, 94.31, H, 5.55).

Preparation of 1,2,4-Triphenylnaphthalene.—2-Bromo-1,1-diphenylethylene (2.59 g.) was added to ether slurried with 3.0 g. of sodium. The mixture was stirred for 2.5 days under a nitrogen atmosphere at room temperature. Methanol was added to the dark red mixture. When the excess sodium was destroyed, the mixture was poured into 300 ml. of water. Ether extraction afforded a residue weighing 1.57 g. This extract was heated to 190–215° with sulfur (3.0 g.) in a closed system swept with nitrogen. Chromatography on acid-washed alumina of the organic products gave 0.744 g. of II. Two crystallizations from methanol were used to give white crystals melting at 160.5–161.5°

Related Thermal Treatments. A. 1,2,3-Triphenylnaphthalene was prepared by the method of Smith and Hoehn.[11] Its melting point was 153–154°. A sample (2.214 g.) was heated in a nitrogen atmosphere to 440–445° for 23 min. After cooling the melt, an infrared spectrum indicated no change. The melting point of the solidified mass was 152–153°. Mass spectral analysis gave one peak at 356.

B.—Compound III (3.59 g.) was heated at 410° for 40 min. in a nitrogen atmosphere. The reaction products were worked up as in the pyrolysis of I. The isolated products were II (0.424 g.) and III (0.504 g.). No IV was detected. The principal product (2.16 g.) was clear viscous oil with the same spectral properties as the second unknown hydrocarbon fraction of the pyrolysis of I.

C.—Compound IV (0.176 g.) was heated to 400° for 30 min. under hydrogen pressure (200 p.s.i., charged). Unreacted IV weighed 0.093 g. The nonketonic material (0.062 g.) had the same spectral properties as the third unknown hydrocarbon fraction of the pyrolysis of I.

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[11] L. Smith and H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1186 (1941).

Mechanism of Ozonation Reactions. Nitrones

RONALD E. ERICKSON[1] AND THOMAS M. MYSZKIEWICZ[2]

Department of Chemistry, Canisius College, Buffalo, New York 14208

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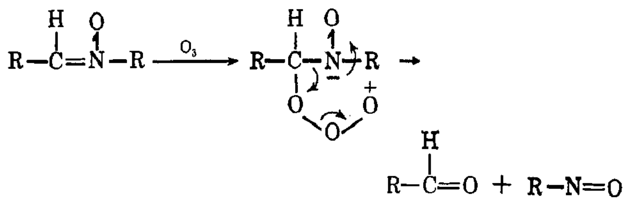
In 1960 Bailey and co-workers studied the reactions between ozone and nitrones and ozone and Schiff bases.[3] From product analysis and a comparison of the relative reactivities of Schiff bases and nitrones (nitrones were much more reactive with ozone) it was suggested that initial ozone attack in both cases was nucleophilic. The suggested mechanism is shown below.



The most obvious method of testing this hypothesis is to determine relative rates of ozonation of appropriately substituted nitrones and Schiff bases. This note reports such a study on nitrones.

The ozonation of nitrones at −78° has been shown by Bailey and co-workers to be quantitative, *i.e.*, no ozone escapes from the reaction flask until the reaction is almost complete. Kinetics on single nitrones with a constant ozone concentration in an ozone–oxygen stream would be expected to be somewhat complex, since one of the products of the ozonation, nitrosobenzene, is also competing for the available ozone. Our interest was not, however, in the absolute kinetic expression but in $(dN_1/dN_2)(N_2/N_1)$ where N_1 and N_2 are appropriately substituted nitrones. Assuming the reaction to be first order in nitrone concentration and any order in ozone concentration

$$-\frac{dN_1}{dt} = k_1(O_3)_s{}^n(N_1)$$

$$-\frac{dN_2}{dt} = k_2(O_3)_s{}^n(N_2)$$

where $(O_3)_s$ is ozone in solution, then

$$\frac{dN_1}{dN_2} = \frac{k_1}{k_2}\frac{N_1}{N_2}$$

and the quantity $(O_3)_s{}^n$ (which varies with nitrosobenzene concentration) is of no concern. Plots of log N_1 *vs.* log N_2 yield the relative rate constant k_1/k_2.

Figure 1 indicates a typical log N_1 *vs.* log N_2 plot while Table I summarizes the data. All of the relative rate constants were determined by least-square statistics and Table I also lists the standard deviation of each relative rate.

TABLE I

RELATIVE RATES OF OZONATION OF *para*-SUBSTITUTED N-PHENYLBENZALDOXIMES IN CHLOROFORM AT −60°

	$k_{p\text{-MeO}}/k_{p\text{-H}}$	$k_{p\text{-H}}/k_{p\text{-Cl}}$	$k_{p\text{-MeO}}/k_{p\text{-Cl}}$
	1.71 ± 0.15	1.54 ± 0.03	2.10 ± 0.07
	2.03 ± 0.17	1.45 ± 0.19	2.28 ± 0.25
Av.	1.9	1.5	2.2

Quantitatively, the results listed in Table I are very disappointing. Standard deviations are as high as 13% and reproducibility is about ±10%. Although the order of reactivity of the substituted nitrones is consistent, the internal consistency is poor in that, arbitrarily assuming that the rates determined relative to hydrogen are accurate, the $k_{p\text{-MeO}}/k_{p\text{-Cl}}$ values should have been 2.85, rather than the experimental value of 2.2. It is also to be noted that the normal σ values for *p*-MeO and *p*-Cl (−0.27 and +0.23, respectively) would have led to the prediction of more equivalent values for $k_{p\text{-MeO}}/k_{p\text{-H}}$ and $k_{p\text{-H}}/k_{p\text{-Cl}}$.

Since the reaction between ozone and nitrones is extremely fast,[4] it is possible that all the data listed

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[1] To whom requests for reprints should be addressed: Chemistry Department, University of Montana, Missoula, Mont.

[2] This work formed part of the M.S. Thesis of T. M. presented to Canisius College, 1964.

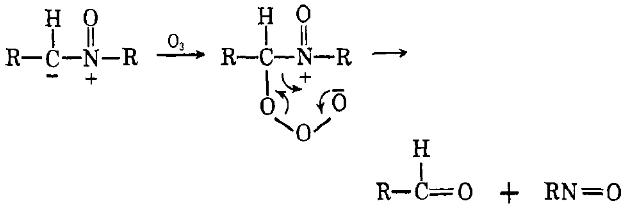
[3] A. H. Riebel, R. E. Erickson, C. J. Abshire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[4] When a cold (−78°) solution of nitrone is added to a saturated ozone solution in Freon 11 at −78°, the deep blue ozone color disappears immediately: D. Bakalik, Senior Thesis, Canisius College, 1965.

in this paper are subject to the limitation of the competitive method of rate determinations as discussed by Tolgyesi.[5] However, our reaction conditions (high concentrations of nitrones, low concentration of ozone, and good stirring action by the ozone-oxygen stream) should have been the most favorable ones possible to avoid this complication.

Despite the deficiencies in the quantitativeness of the data, we feel that the over-all results are significant. The rate sequence p-MeO > p-H > p-Cl leaves little doubt that the course of the ozonation of nitrones involves electrophilic attack of ozone rather than nucleophilic attack.

Electrophilic ozone attack on nitrones is best rationalized by Bailey's alternate mechanism,[3] as follows.



Nucleophilic ozone attack has also been suggested for ozonation of Schiff bases,[3] 2,4-dinitrophenylhydrazones,[6] aldehydes,[7] and certain N-heteroaromatic systems.[8] Relative rate studies on Schiff bases and aldehydes will be published shortly.

Experimental Section

Materials.—Nitrones were prepared from the corresponding aldehydes (Eastman Reagent Grade) and phenylhydroxylamine[9] according to the method of Wheeler and Gore.[10]

N-Phenylbenzaldoxime, m.p. 112° (lit.[11] m.p. 112°), N-phenyl-p-methoxybenzaldoxime, m.p. 115° (lit.[10] m.p. 116°), N-phenyl-p-chlorobenzaldoxime, m.p. 152° (lit.[12] m.p. 153°), and N-phenyl-p-nitrobenzaldoxime, m.p. 184° (lit.[13] m.p. 182°) were the nitrones used in the study.

Ozonations.—The ozonations were carried out using a Welsbach T-23 ozonator and ozonation flasks of the type described by Bailey.[14]

Equal molar quantities (~0.02 mole) of two different nitrones were dissolved along with a known amount of m-nitrotoluene (internal standard) in 75 ml. of chloroform and ozonized with an ozone-oxygen stream (~100 mg. of ozone/l.) at −60° until almost 2 mole equiv. of ozone was absorbed. Samples (0.5 ml.) were taken at 8–12-min. intervals and chromatographed as described later.

Some data were also obtained at −78° in methylene chloride, but since the p-chloronitrone was insoluble under these conditions, further work was not carried out.

The compound N-phenyl-p-nitrobenzaldoxime was insoluble in all useful solvents at temperatures which would have been appropriate for relative rate studies.

Ozonation of Internal Standard, m-Nitrotoluene.—A 0.25 M solution (20 ml.) of m-nitrotoluene (0.005 mole) in methylene chloride was ozonized at −78° with an excess of ozone (0.010 mole). Samples before and after ozonation were chromatographed and identical areas were obtained. m-Nitrotoluene was thus judged suitable for use as an internal standard.

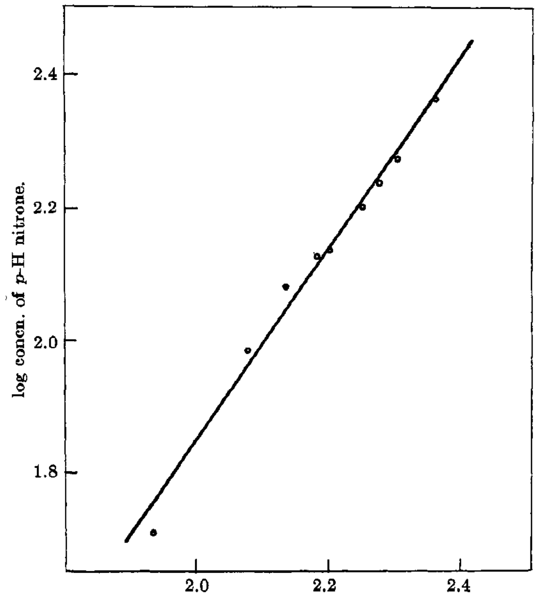


Figure 1.—Log concentration of p-H nitrone *vs.* log concentration of p-Cl nitrone. The slope $k_{p\text{-H}}/k_{p\text{-Cl}}$ is 1.45.

Competing Reactions.—Ozonation of the aldehydes to acids or, particularly in the case of p-methoxy substituents, ozonation of the aromatic rings, would invalidate the analytical method used. Previous work indicated that aldehydes react much more slowly than nitrones and in a typical kinetic run involving p-methoxy-substituted nitrones, 96% of the original concentration of nitrone was accounted for as aldehyde near the end of the reaction. Thus, neither aldehyde nor ring ozonation was a serious problem.

Analytical Method.—All analytical data were obtained *via* vapor phase chromatography on a Perkin-Elmer 154B vapor fractometer with external Variac-controlled injection-block temperature. The most satisfactory column was a 40% silicone grease on 30–60 mesh Chromosorb P described by Carson and Miller.[15]

Typical gas chromatographic conditions were oven temperature, 110°; flow rate, 145 cc./min.; injection-block voltage, 10 v.; sample size, 10 μl.; and recorder range, 1. The low oven temperature and low injection-block voltage were necessary to avoid the decomposition of nitrones on the block or in the oven. Under these conditions only the products of the ozonation (aldehydes, nitrobenzene, and nitrosobenzene) and the internal standard were chromatographed.

Samples for the calibration curves were prepared using 25-ml. volumetric flasks and chloroform as the solvent. Five chromatograms were obtained for each sample and their areas were determined by use of a compensating polar planimeter. The average of the five areas was taken for that particular concentration and standard curves were determined.

Between 7 and 15 samples were used for each kinetic run, with each sample injected into the chromatograph as soon as possible after sampling. Areas of the aldehydes and internal standards were determined by use of the planimeter and, after standardization, the concentrations of aldehydes were determined from the standard curves. Nitrone concentrations were then obtained for each sample by subtracting the aldehyde concentration from the known initial nitrone concentration.

Relative rate constants were determined by plotting log N_1 *vs.* log N_2 and determining the slope by the least-squares technique.

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