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The Removal of Organic Material from Recycle Nitric Acid by Ozone

Walter E. Clark
W. B. Howerton

~~APPLIED TECHNOLOGY~~

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THE REMOVAL OF ORGANIC MATERIAL FROM RECYCLE NITRIC ACID BY OZONE

Walter E. Clark
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Date Published: April 1979

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THE REMOVAL OF ORGANIC MATERIAL FROM RECYCLE NITRIC ACID BY OZONE

Walter E. Clark
W. B. Howerton

ABSTRACT

Organic compounds can be removed from recycle nitric acid (e.g., 2.5 to 10 M HNO₃) by ozonation. In the absence of catalysts the removal of acetic acid, one of the most resistant of the aliphatic species, was found to be slower than its removal from distilled water under similar conditions. At 95°C, about 8 hr was required to reduce the carbon content of a 10 M HNO₃ solution from 100 µg/ml to 10 µg/ml in the absence of catalysts. However, the same reduction was accomplished in only about 1 hr when silver ion was added at a concentration of 50 mg/liter.

Silver ion (Ag⁺) is the most effective of the catalysts tested for removal of acetic acid from 2.5 to 10 M HNO₃ by ozonation. Other, less efficient catalysts include Pd²⁺, Mn²⁺, Fe³⁺, and silica gel.

The initial stages of the reaction in nitric acid appear to be first order with respect to the acetic acid concentration when no catalyst is present. Average rate constants are $1.75 \times 10^{-5} \text{ sec}^{-1}$ at 75°C, $4.50 \times 10^{-5} \text{ sec}^{-1}$ at 85°C, and $1.02 \times 10^{-4} \text{ sec}^{-1}$ at 95°C. The pseudo activation energy calculated from an Arrhenius plot of these data is about 27 kcal/mole.

1. INTRODUCTION

The presence of organic material in dissolver and other process solutions has caused difficulty since the earliest days of nuclear fuel reprocessing. Most of the initial concern stemmed from the interference of solvent degradation products with the separation of fissionable material from fission products.¹ This problem is of even

greater significance in the light of current considerations since future rules and regulations will almost certainly require more thorough removal of radioiodine from process gases and solutions than was necessary in previous practice.

Even small (trace) amounts of unidentified organic materials can have a markedly deleterious effect on the separation of radioiodine from both reprocessing solutions and off-gases, including those resulting from reactor accident conditions.²⁻⁴ This effect is caused by the iodination of the organics to form iodo-compounds which are not amenable to the techniques commonly used for the quantitative separation of iodine. Thus, when iodine is to be removed from process solutions by volatilization as I_2 , a small fraction that is attached to relatively high-boiling organic impurities may be resistant to this treatment while another fraction will be present as methyl iodide (CH_3I), which is not as easily removed from gas streams as is I_2 .⁵ No realistic explanation has been offered as to why there should be a lower limit on the amount of organic material required to produce such effects; in fact, no lower limit has been observed. The trace of organic material present in reagent-grade nitric acid has been shown to result in the formation of methyl iodide; the amount of organic material present in the case reported⁶ was estimated to be equivalent to 0.1 ppm ($\mu\text{g/ml}$) of acetic acid, or an organic carbon concentration of 0.04 $\mu\text{g/ml}$. These results are generally consistent with those obtained by Schmitt⁷ at ORNL, who found that the unplanned volatilization of iodine from nitric acid solutions could be eliminated only by very vigorous oxidative treatment of all reagents prior to use. Studies of the reaction indicate that the formation of organic iodide is related to the $I^0 \rightarrow IO_3^-$ oxidation step.^{8,9} In a radiation field, the iodination reaction would be the same as, or closely related to, the types of reactions responsible for the radical-scavenging effect observed with I_2 in studies of the radiolysis of hydrocarbons.¹⁰

Ideally, organic materials should be removed from a process solution in such a manner that no extraneous chemical substances are introduced into the solution. If oxidation is used, this limits the reagents to oxygen, hydrogen peroxide, or ozone; it is also possible

that electrolysis could be used. Oxidation by molecular oxygen of relatively stable organic compounds such as acetic acid in aqueous media requires high temperatures and pressures. Experimental work has shown that, although this method is effective,¹¹ the necessity of using high-pressure equipment makes it unattractive if suitable alternatives are available. Hydrogen peroxide is a strong oxidizing agent that is widely used in a variety of commercial and industrial applications; however, unless reaction rates are rapid, its decomposition is likely to occur before reaction is complete. One possible solution might be to feed the reagent in at a slow but continuous rate. Results of our scoping tests with peroxide were not encouraging. The practicality of electrolysis as a method for oxidizing a variety of organic compounds is very doubtful.

Ozonation is the most attractive possibility of the oxidative treatments considered. Ozone has a theoretical oxidation potential of 2.07 V in acid solution vs 1.77 V for hydrogen peroxide. Considerable experience has been reported in its use with various organic compounds.^{12,13} If effective in removing organic material, ozonation will lend itself readily to the purification of a liquid which is to be held in a storage container for an extended period. If the nitric acid solution must also be sparged by an air stream during storage (e.g., the Iodex decay tank), the use of ozone may be even more advantageous, particularly since it will prevent volatilization of iodine by reoxidizing radiolytic nitrite to nitrate and free iodine to iodate. Simultaneously, any traces of chloride present will be oxidized to chlorine, which will concurrently be sparged from the acid solution.

The purpose of the work reported here was to develop a method for removing trace quantities (<100 µg/ml carbon) of organic material from recycle acid by oxidation with ozone. The procedure and equipment used in the various experiments are described in Sect. 2. The results are presented, both graphically and in tabular form, in Sect. 3 and discussed in Sect. 4.

2. EXPERIMENTAL PROCEDURES

Stirred solutions containing known amounts of acetic acid* were sparged with a stream of ozonized oxygen, and the off-gas was routed successively through drying tubes and Ascarite traps in order to determine the amount of CO_2 formed (see the experimental setup in Fig. 1). When the weight gain of the latter indicated that the reaction was approaching completion, the experiment was concluded and the data were used in making a material balance for carbon. The O_3 content was measured periodically both in the incoming sparge gas and in the off-gas in order to determine the constancy of output from the ozone generator and to estimate the percentage of the O_3 actually used in oxidizing the acetic acid.

Carbon dioxide was determined periodically by direct weighing of the Ascarite absorption tubes. Ozone was determined by back titration of the KI solution used in the O_3 traps with thiosulfate. Flows were regulated to approximate values by the use of flowmeters in each gas stream; however, the total flows as shown by the wet-test meters were used for the purpose of calculating material balances.

In early experiments, acetic acid in the starting and final pot solutions was determined by means of a Packard Model 7300 gas-liquid chromatograph. However, this method was not sufficiently sensitive to determine acetic acid accurately in 10 M HNO_3 when the carbon content had decreased to less than $\sim 10 \text{ } \mu\text{g/ml}$.

An intensive effort was made to determine carbon levels below $10 \text{ } \mu\text{g/ml}$ in 10 M HNO_3 by use of a Model 915A Beckman Total Carbon Analyzer. Unfortunately, the results were erratic and unpredictable despite help and advice from the manufacturer. The machine suffered from severe instability problems when undiluted nitric acid samples

*Acetic acid was chosen because it is among the most oxidation-resistant of all aliphatic compounds and because it represents the simplest highly resistant aliphatic compound in the oxidation-degradation process. Certain aromatic compounds are more resistant to oxidation than acetic acid, but the chance that they would be present in the system is remote.

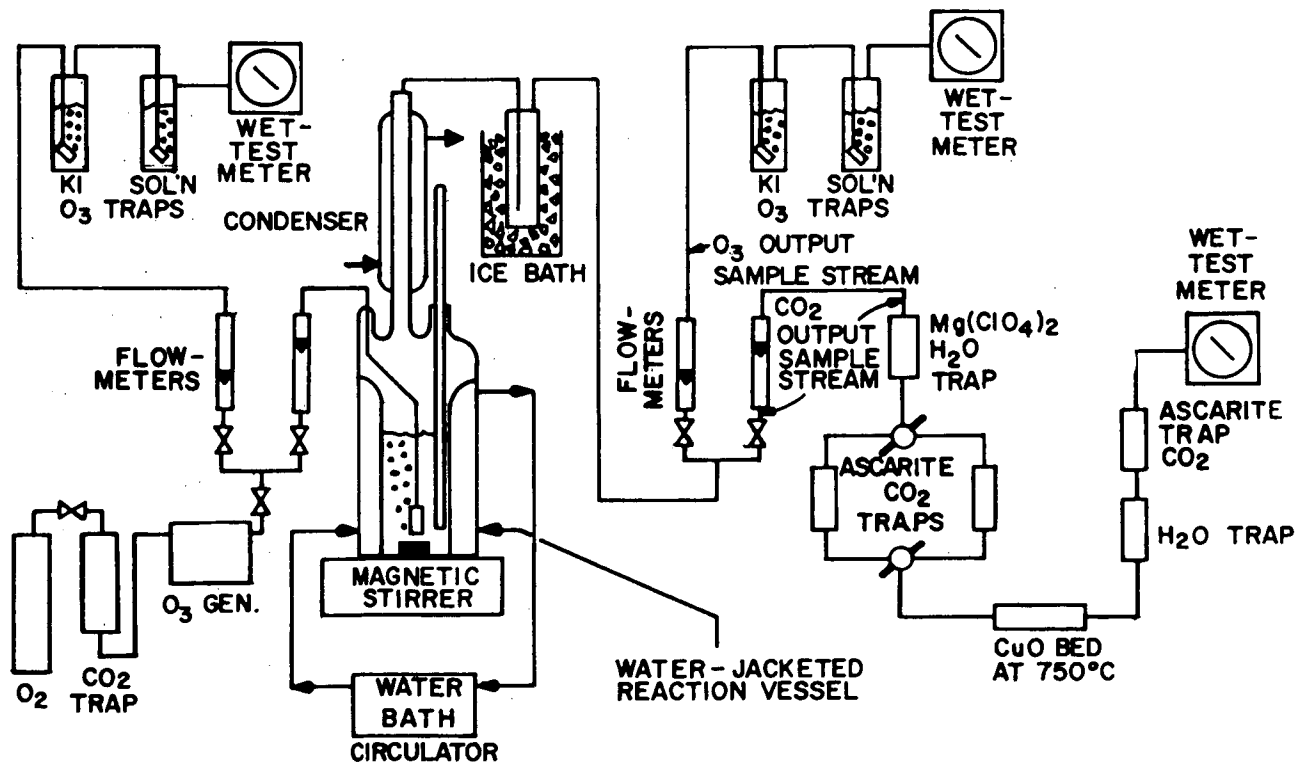


Fig. 1. Apparatus for studying the removal of organic material from aqueous solutions by ozone.

were inserted. When we attempted to eliminate these problems by using samples that were appropriately diluted, the accuracy decreased unacceptably. Therefore, the material balance method of operation was employed in an attempt to obtain data plots which could be extrapolated to zero carbon content, thus eliminating the need for supersensitive analyses.

The ozone generator used in these experiments was a Marine Water Purifier, Model C2P-3C, manufactured by Pollution Control Industries, Inc. When operating at maximum power with a flow of 250 cc/min of oxygen, the output stream usually contained O_3 at a concentration between 82 and 89 mg/liter. Most of the experiments reported here were run using a flow of 250 cc/min of oxygen through the ozonizer, of which 200 cc/min was then routed through the 200-cc reaction pot. and 50 cc was diverted to the ozone analysis train (Fig. 1).

The solution to be purified consisted of either distilled water or nitric acid, 2.5 M or 10 M, containing a measured amount (usually a carbon content of ~ 50 $\mu\text{g/ml}$) of acetic acid. In the earlier experiments, we used stock solutions prepared from water and nitric acid that had been thoroughly ozonized. Because the kinetic plots often failed to pass through the origin, the water or nitric acid for later experiments was ozonized in the reaction vessel immediately before the addition of the acetic acid until there was no further weight gain by the Ascarite tube. This corrected the discrepancy in most cases, indicating that the irregularity was due to a trace of organic matter present in the reaction vessel or introduced along with the stock solution. After difficulty had been experienced with CO_2 contamination of one of the tanks of oxygen used, a drying column filled with Ascarite was inserted into the gas line between the oxygen tank and the ozonizer. (However, this was not usually necessary.) When a catalyst was used, it was added to the solution before ozonation.

A solution volume of 200 ml was used in all except the very early experiments. The temperature of the solution was usually 85°C , although some data were also obtained at 95, 75, and 40°C , as explained below. No experiments were performed with solutions containing simulated fission products since the objective of this work was to remove

only the small amounts of organic materials that will remain after the acid has been subjected to at least one "recycle" distillation. Chloride ion, at a concentration of 100 $\mu\text{g/ml}$, was present in a few of the silver-catalyzed experiments run at 85°C. The chlorine was quantitatively sparged from the ozonized system in less than 15 min without measurably affecting the rate of oxidation of the acetic acid.

3. RESULTS

The data show that acetic acid is oxidized more slowly by ozone in 2.5 and 10 M HNO_3 than in distilled water as long as no catalyst is present (Fig. 2). Relatively little difference is observed between the rates in 2.5 M HNO_3 and 10 M HNO_3 , except that the latter are slightly more rapid.

The addition of Ag^+ catalyst markedly increases the rate in HNO_3 , while the rate in water is increased only very slightly (Fig. 3). The action of the silver apparently involves formation of a higher oxide (i.e., either AgO , Ag_2O_3 , or both) since a dark coloration appears in the ozonized HNO_3 after essentially all organic material has been removed by oxidation. The reaction rate increases rapidly with the concentration of Ag^+ up to about 50 mg/liter (0.464 meq), but more slowly with higher concentrations (Figs. 4 and 5).

Palladium(II) and Mn^{2+} , while less effective than Ag^+ , are also positive catalysts for the ozonation reaction (Fig. 6). Silica gel, precipitated by the addition of a small amount of sodium silicate (water glass) solution, and Fe^{3+} have even smaller positive catalytic effects. Other candidate catalysts tested--- Cu^{2+} , Co^{2+} , Ce^{3+} , and Cr^{3+} ---were ineffective when employed in concentrations of up to 1 g/l. Cobalt(II), the only one of these tested at concentrations greater than 1 g/l, did show positive results when present at the impractically high level of 19.5 g/l (0.33 M).

An experiment to determine the effect of varying the O_3 concentration in the sparge gas was performed only in a water solution, and the work was not extended to HNO_3 . The results showed a trend toward a

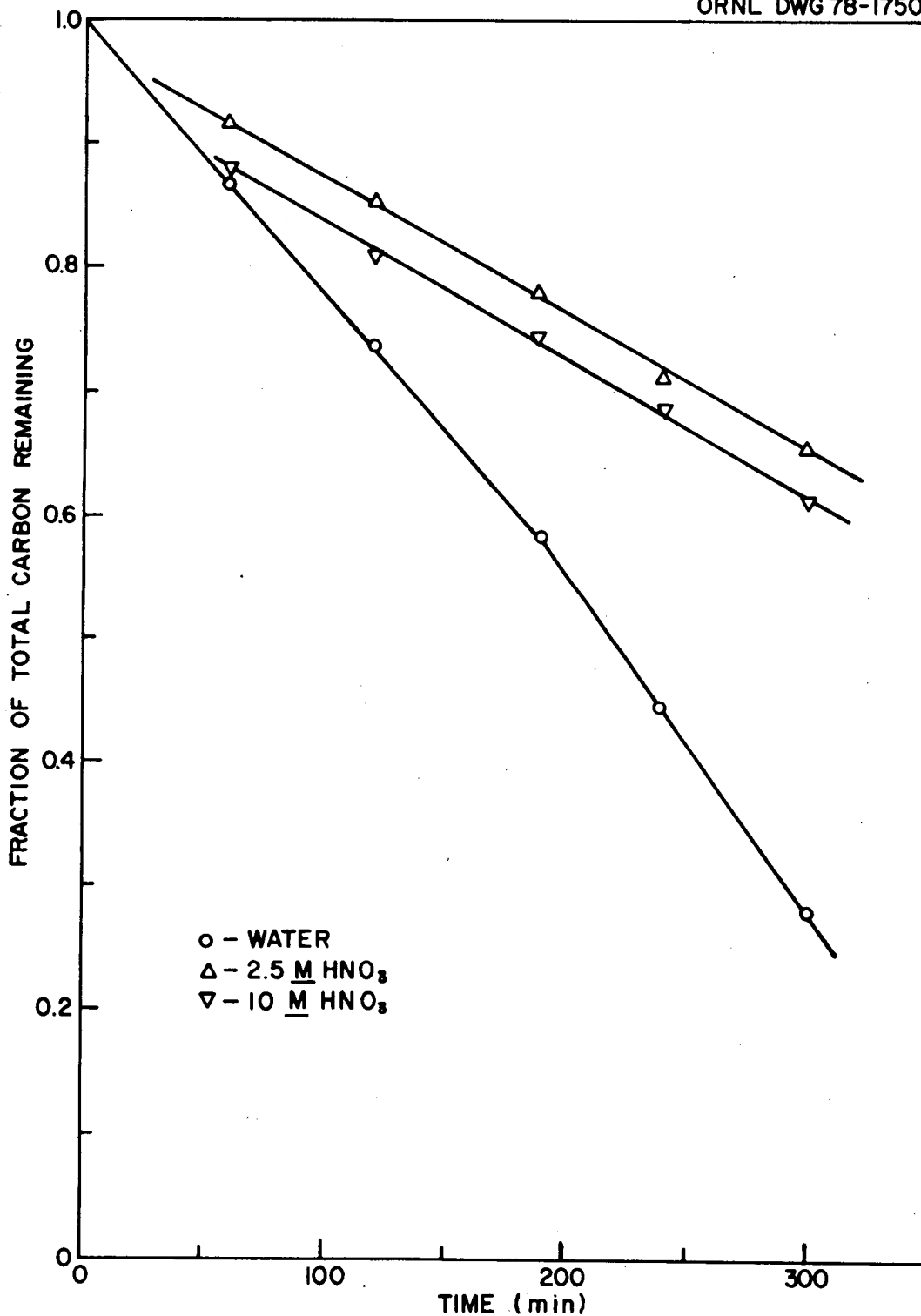


Fig. 2. Comparison of the ozonation rates of acetic acid in water and in 10 M and 2.5 M HNO₃ at 85°C with no catalyst.

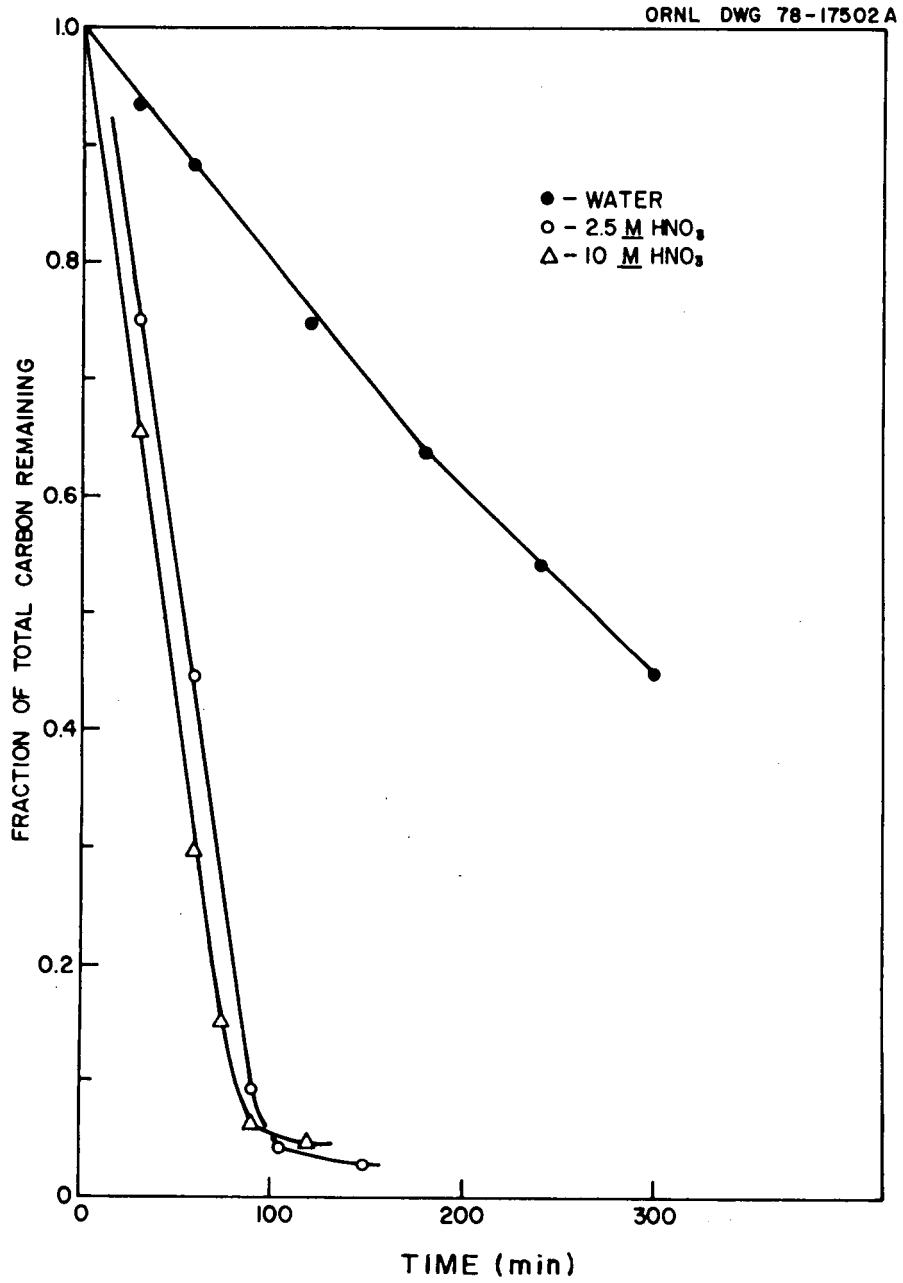


Fig. 3. Comparative effects of Ag^+ catalyst (50 mg/l) on the ozonation of acetic acid in water and in 10 M and 2.5 M HNO_3 at 85°C.

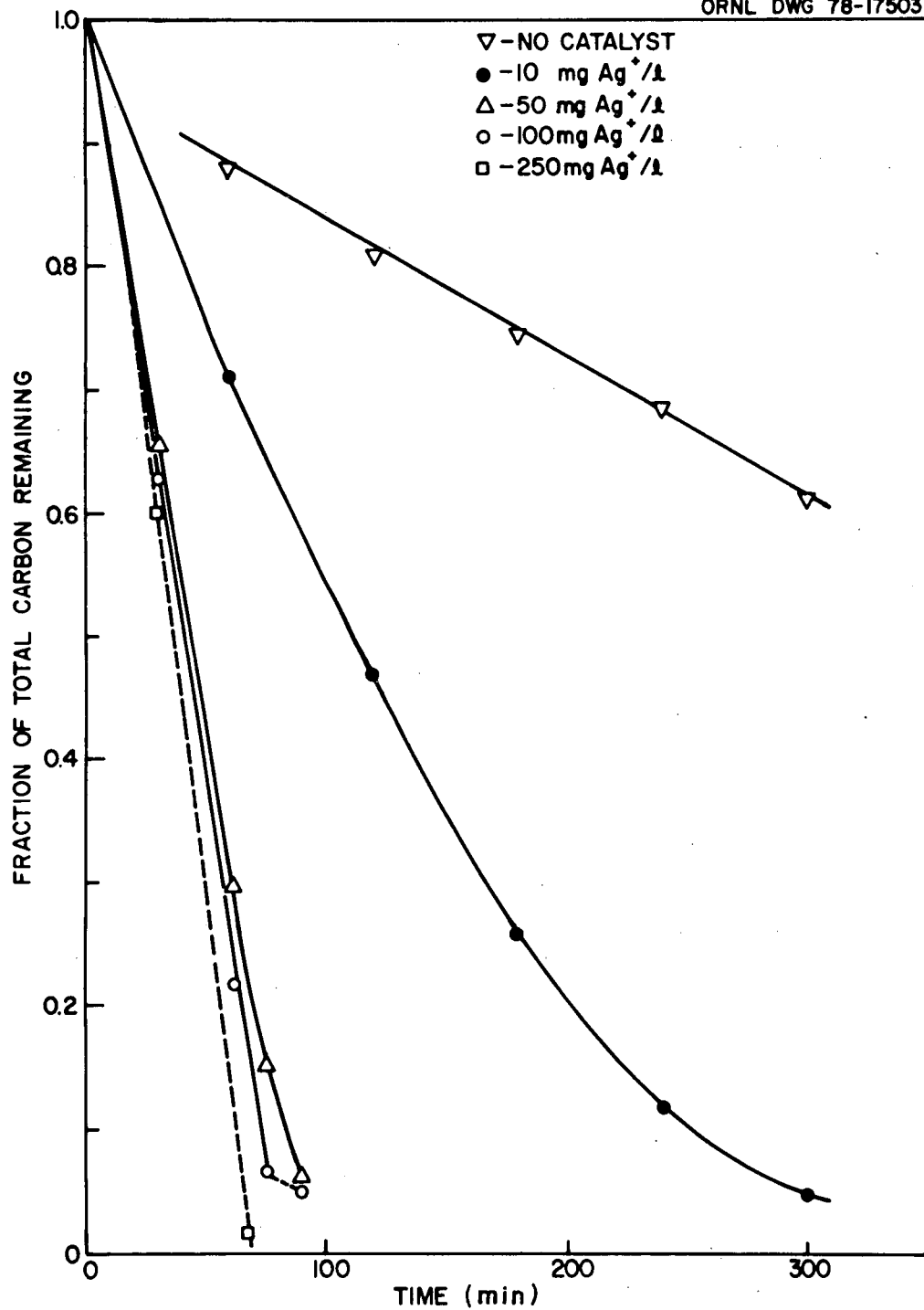


Fig. 4. Effect of Ag⁺ concentration on the ozonation of acetic acid in 10 M HNO₃ at 85°C.

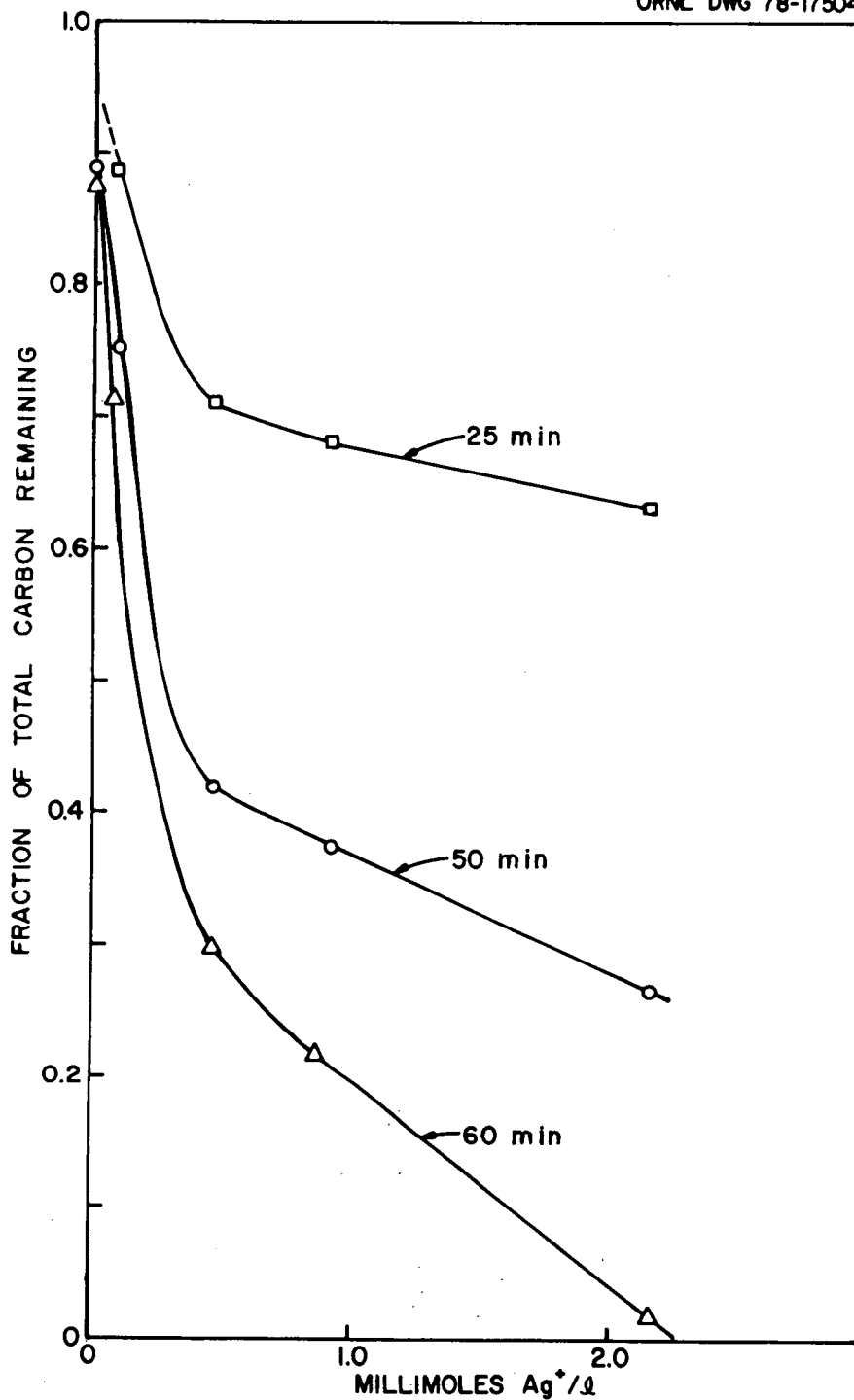


Fig. 5. Effect of Ag⁺ concentration on the ozonation of acetic acid in 10 M HNO₃ at 85°C at various reaction times. Intermediate points on these curves were obtained from data plots.

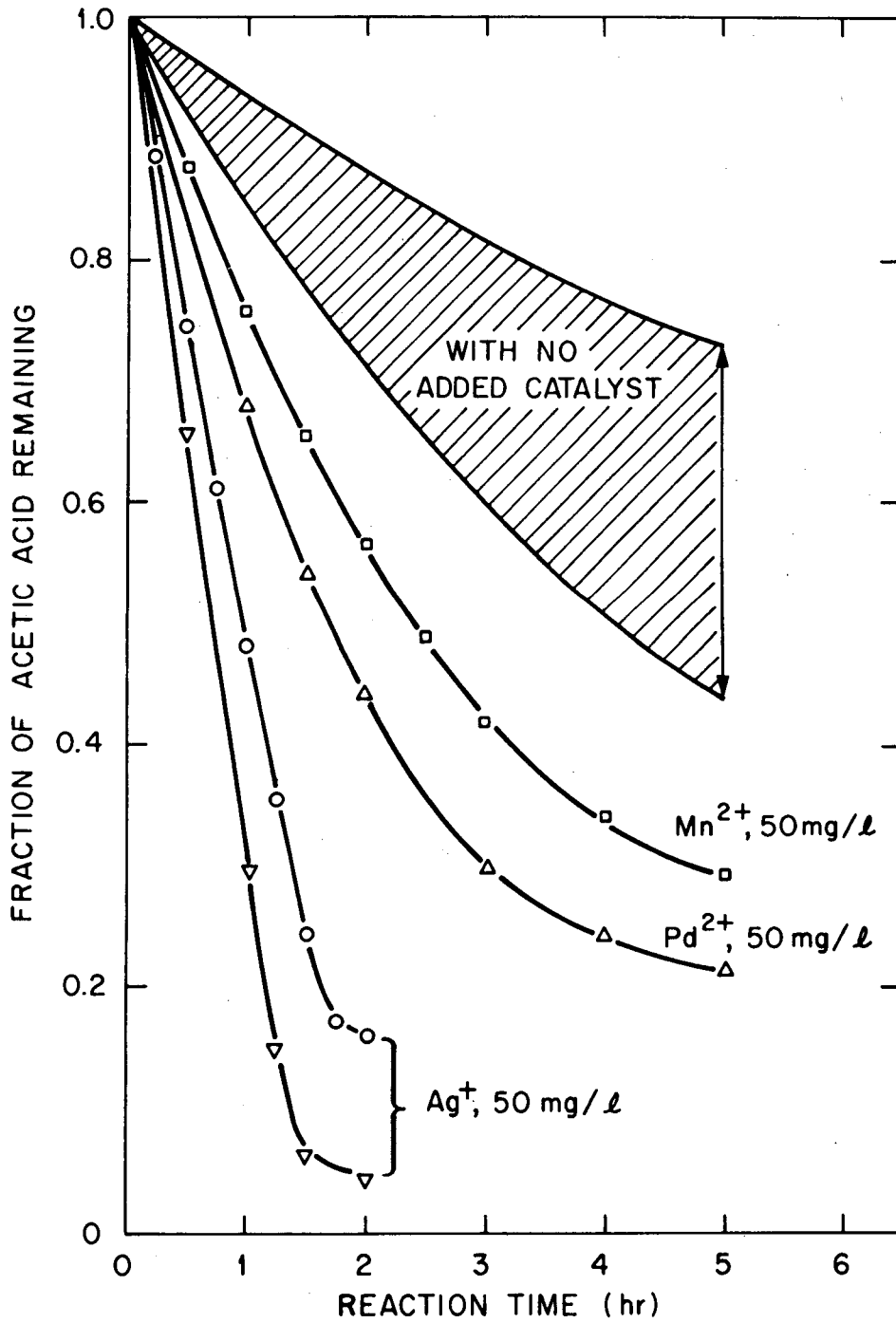


Fig. 6. Relative effects of various catalysts on the removal of acetic acid from 10 M HNO_3 by ozonation at 85°C.

somewhat slower reaction as the O_3 content was decreased, but the data were not consistent. Carefully controlled variation of O_3 content was difficult with the equipment used. In addition, the uncatalyzed reaction was so slow that the difference in O_3 contents of the entering and leaving gas streams was not analytically significant.

An undesirable amount of scatter is evident in the results (e.g., curve for no added catalyst, Fig. 6), particularly those for the earlier experiments. Even when great care was taken to ozonate the solution at temperature for several hours before the acetic acid was added, an occasional experiment yielded up to 18% more CO_2 than could be accounted for by the acetic acid alone. Placing an Ascarite trap between the oxygen tank and the ozonizer did not eliminate this phenomenon. The data reported in Table 1 include some anomalous results which we cannot explain; however, data from experiments in which known perturbations occurred have been omitted.

As expected, the reaction rate in 10 M HNO_3 is highly temperature-dependent. At 25°C, the reaction was too slow to make measurement practical under our experimental constraints; at 40°C, the normal experimental scatter was still so great that our results are considered to be unreliable. Data from experiments at 95, 85, and 75°C are compared graphically in Fig. 7.

Results of an experimental run with only one-fourth the usual concentration of acetic acid (No. 20) almost exactly duplicated those obtained in an experiment with the usual concentration (Fig. 8) when the data were plotted in the conventional manner for a reaction which is first order with respect to acetic acid concentration. This indicates that the primary step in the ozonolysis of acetic acid is probably first order with respect to the concentration of acetic acid. This, in turn, justifies calculation of first-order rate constants for the reaction from the initial slopes of these plots. The average values of the rate constants, as determined from our data, were $1.75 \times 10^{-5} \text{ sec}^{-1}$ at 75°C, $4.50 \times 10^{-5} \text{ sec}^{-1}$ at 85°C, and $1.02 \times 10^{-4} \text{ sec}^{-1}$ at 95°C. An Arrhenius plot of these data (Fig. 9) has a slope which corresponds to an activation energy of about 27 kcal/mole.

Table 1. Removal of acetic acid from H₂O and HNO₃ by ozonation

Expt. No.	Solution	Temp. (°C)	Catalyst		Approx. O ₃ Conc. (g/l)	Fraction of carbon remaining in solution after reaction time (min) of:												
			Type	Conc. (mg/l)		15	30	45	60	75	90	105	120	150	180	210	240	300
1	H ₂ O	85	None		88.6				0.850		0.647		0.412		0.214	0.038		
2	H ₂ O	85	None		43				0.905		0.791		0.665		0.522	0.416		
3	H ₂ O	85	None		77.6				0.885		0.670		0.459		0.265	0.068		
4	H ₂ O	85	None		83.6				0.866		0.735		0.583		0.445	0.279		
5	H ₂ O	85	Ag ⁺	10	85.2				0.850		0.696		0.554		0.429	0.308		
6	H ₂ O	85	Ag ⁺	10	83.2				0.858		0.730		0.636		0.565	0.501	0.434	
7	H ₂ O	85	Ag ⁺	50	86.8		0.935		0.884		0.748		0.638		0.541	0.449		
8	2.5 M HNO ₃	85	Ag ⁺	100	82.4		0.829		0.662	0.504	0.358	0.228	0.113	0.040	0.016			
9	2.5 M HNO ₃	85	None		81.7				0.810		0.720		0.631		0.555	0.475		
10	2.5 M HNO ₃	85	None		85.6				0.917		0.854		0.780		0.710	0.656		
11	2.5 M HNO ₃	85	None		80.0				0.910		0.837		0.777		0.724	0.670		
12 ^a	2.5 M HNO ₃	85	Ag ⁺	10	83.0				0.720		0.429	0.270	0.133	0.041	0.0			
13 ^a	2.5 M HNO ₃	85	Ag ⁺	10	80.5		0.854		0.712	0.563	0.421	0.275	0.143	0.057	0.048	0.032		
14	2.5 M HNO ₃	85	Ag ⁺	50	87.2		0.752		0.445	0.094	0.043	0.028						
15	2.5 M HNO ₃	85	Ag ⁺	50	92.2	0.846	0.683	0.506	0.327	0.150	0.005							
16	2.5 M HNO ₃	85	Ag ⁺	100	95.2		0.678		0.267	0.042	0.030	0.023						
17	10 M HNO ₃	85	None		82.5				0.817		0.709		0.596		0.508	0.433		
18	10 M HNO ₃	85	None		92.6				0.880		0.808		0.744		0.684	0.611		
19	10 M HNO ₃	85	None		81.8				0.932		0.874		0.812		0.768	0.733	0.714	0.683
20 ^b	10 M HNO ₃	84	None		-		0.926		0.863		0.784		0.712		0.651	0.584		
21 ^a	10 M HNO ₃	85	Ag ⁺	10	84.9				0.712		0.468							
22	10 M HNO ₃	85	Ag ⁺	50	83.4		0.655		0.296	0.151	0.061	0.046						
23	10 M HNO ₃	85	Ag ⁺	100	83.0		0.63		0.217	0.066	0.050							
24 ^b	10 M HNO ₃	84	Ag ⁺	250	-		0.677		0.205	0.173	0.0							
25	10 M HNO ₃	85	Fe ⁺	1000	85.4				0.820		0.665		0.528		0.421			
26	10 M HNO ₃	85	Cr ³⁺	1000	88.8				0.983		0.954		0.939		0.934	0.926		
27	10 M HNO ₃	85	Ce ³⁺	100	84.3				0.948		0.913		0.889		0.875			
28	10 M HNO ₃	85	Mn ²⁺	50	85.0		0.875		0.755	0.651	0.565	0.486	0.419		0.339	0.287		
29	10 M HNO ₃	85	Cu ²⁺	1000	86.6				0.893		0.774		0.669		0.602	0.571		
30	10 M HNO ₃	85	Cu ²⁺	1000	84.8				0.884		0.789		0.708		0.643	0.593		
31	10 M HNO ₃	85	Pd ²⁺	50	82.5				0.678	0.542	0.441		0.296		0.241	0.215		
32 ^c	10 M HNO ₃	85	Si gel		82.5		0.868		0.782		0.658		0.549		0.456	0.369		
33	10 M HNO ₃	75	Co ²⁺	1000	84.1				0.894		0.804		0.740		0.700	0.684		
34	10 M HNO ₃	75	None		-				0.936		0.890		0.841		0.793	0.759	0.724	0.684
35	10 M HNO ₃	85	None		-				0.940		0.896		0.851		0.812	0.777	0.738	0.705
36	10 M HNO ₃	95	None		-				0.837		0.681		0.535		0.408	0.302	0.203	0.121
37	10 M HNO ₃	95	None		-				0.837		0.711		0.574		0.458	0.351	0.253	0.171
38 ^{a,d}	10 M HNO ₃	95	Ag ⁺	50	-	0.829	0.612	0.397	0.193	0.06	0.036	0.012	0.0					

^aMaterial balances for carbon in these experiments were high by more than 5%. Data listed are for the amount found (i.e., the greater amount).

^bAnalytical data by gas chromatography. Solutions contained 50 µl of glacial acetic acid per liter of solution.

^c3 ml of "water glass"/200 ml solution. This is equivalent to 0.88 g of Na₂O--1.5 SiO₂.

^dOn the basis of acetic acid added, carbon in the solution would have been entirely removed after about 72 min. Material balance for carbon was about 12% high.

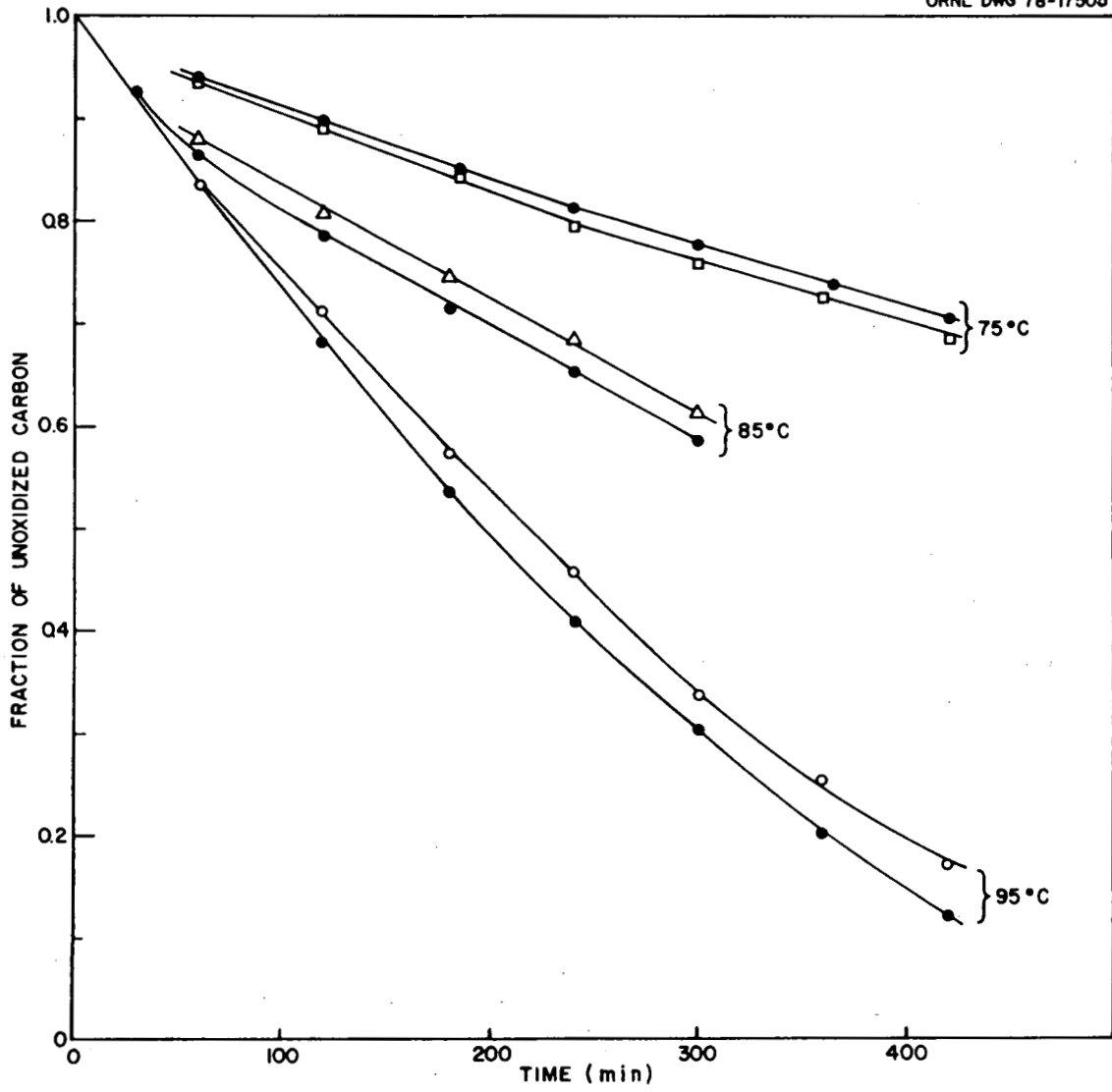


Fig. 7. Effect of temperature on the removal of acetic acid from 10 M HNO_3 by ozonation in the absence of catalysts.

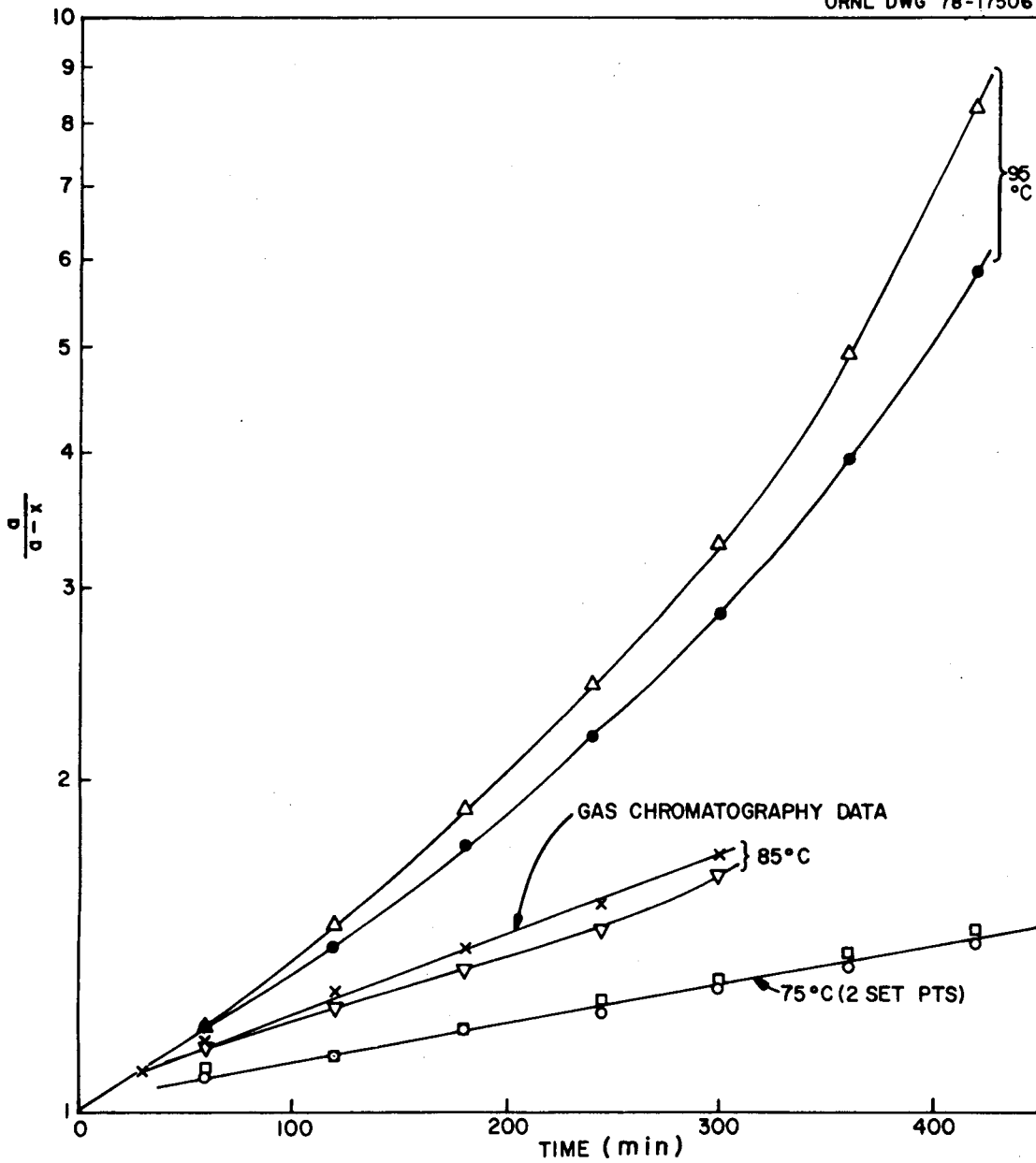


Fig. 8. First-order kinetic plots of the ozonation of acetic acid in 10 M HNO_3 at 75, 85, and 95°C.

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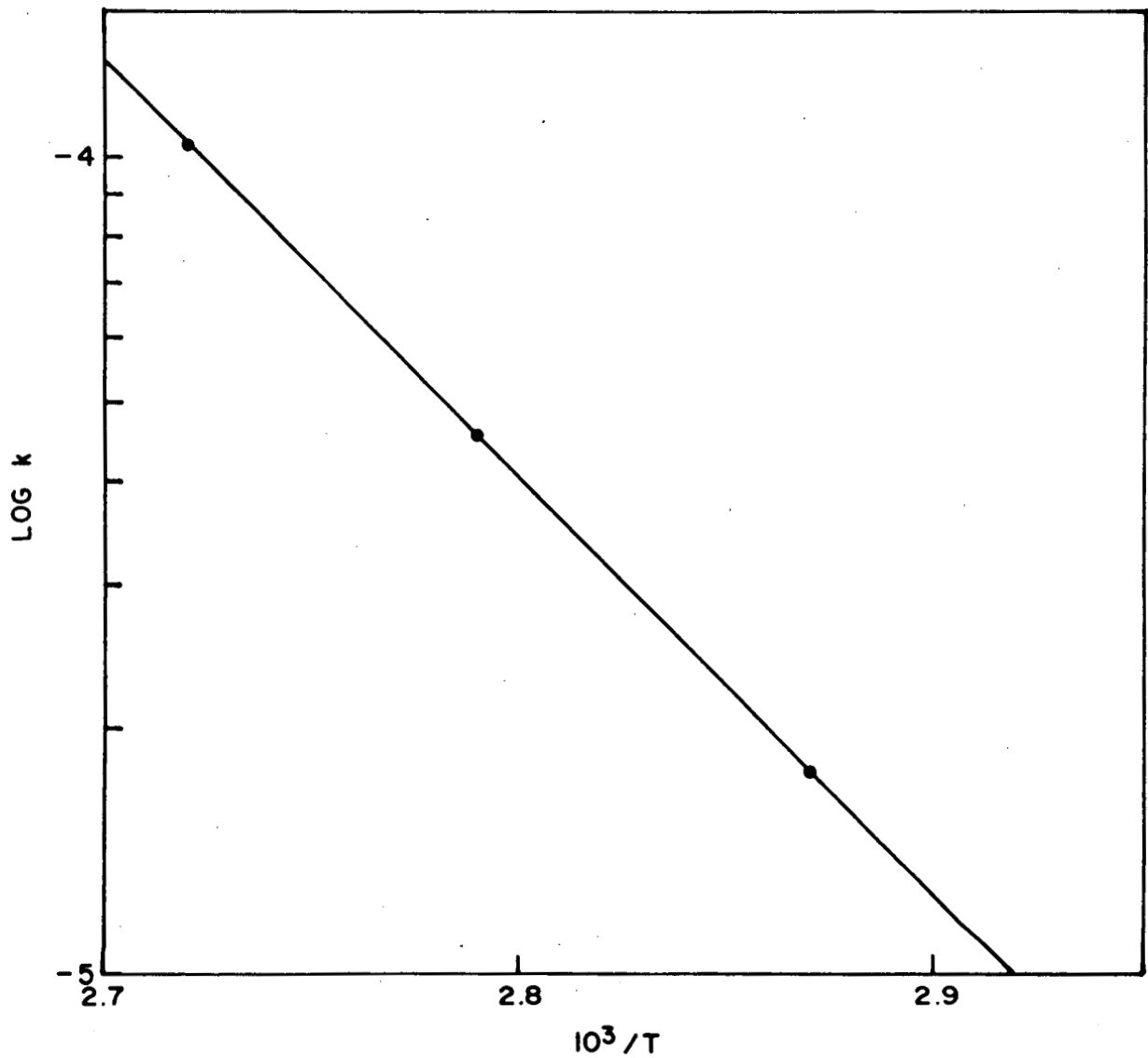


Fig. 9. Arrhenius plot of data from the uncatalyzed reaction of ozone and acetic acid in 10 M HNO₃ at 75, 85, and 95°C.

Two experiments were run at 95°C in order to establish the shortest time in which the acetic acid would be removed from 10 M HNO₃ by ozonation when Ag⁺ catalyst was present at a concentration of 50 mg/ℓ. The data obtained in these experiments showed that acetic acid was removed to a level of 10% of its initial value in slightly more than 1 hr; and, in one instance, an apparent level of zero was reached in ~70 min. The results of these experiments are compared in Fig. 10 with those obtained at 85°C in the presence of Ag⁺ catalyst and also with those of an uncatalyzed experiment at 95°C.

4. DISCUSSION

The results of this study show that even acetic acid can be removed from recycle HNO₃ by ozonation at elevated temperatures in the presence of a catalyst. Because of the difficulty of determining carbon levels below 10 µg/ml in HNO₃, we were not able to obtain kinetic data which can be unequivocally extrapolated to zero carbon content. Determination of exact values in the range of 0 to 10 µg/ml will require further development of analytical methods.

Literature references indicate that acetic acid is almost inert to ozone at ambient temperatures. Glacial acetic acid has, in fact, been employed as a solvent for studies of the ozonolysis of other organic species. According to Paillard and Emile Briner,¹⁴ who found a very slight attack, glacial acetic acid is first converted into peracetic acid. Even traces of water tend to decompose this compound to regenerate acetic acid with the simultaneous formation of hydrogen peroxide. Assuming that the reaction in HNO₃ occurs by the same or a similar mechanism, the back reaction may be responsible for much of the observed deviation from first-order kinetics. Investigation of the reaction mechanism is beyond the scope of this study.

No claim is made for high accuracy in the determination of the pseudo energy of activation. The calculation was made in order to allow approximate estimation of the values of k at lower temperatures, assuming that the indicated first-order kinetics are correct.

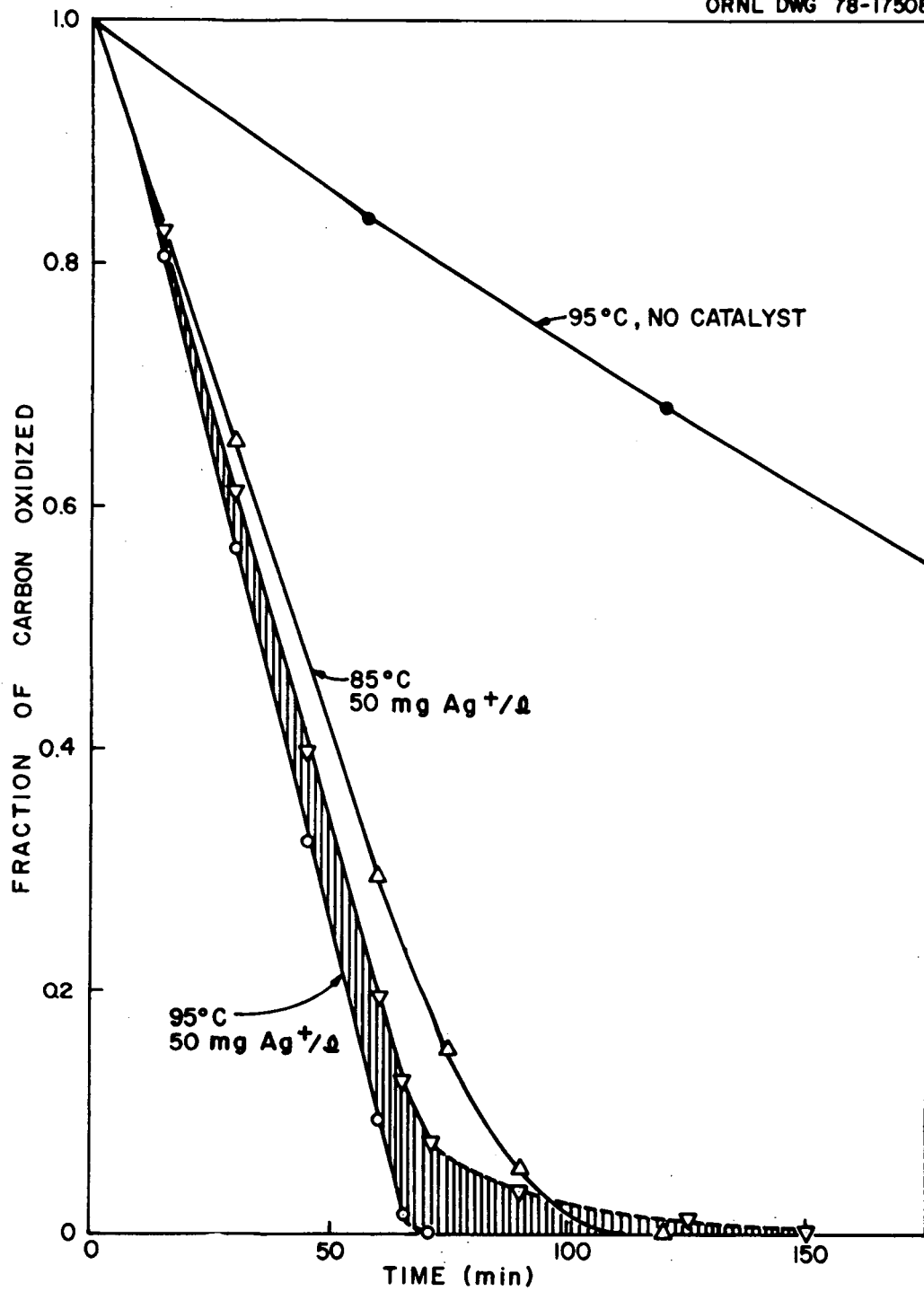


Fig. 10. Comparison of the catalyzed ozonation of acetic acid in 10 M HNO₃ at 95°C with the uncatalyzed reaction at 95°C and the correspondingly catalyzed reaction at 85°C.

If this process is adapted for plant-scale use, the employment of fission product silver as a catalyst may prove to be cost effective. Recovery and recycle of the catalyst should be relatively simple and straightforward in any case. The presence of a trace of fission product ruthenium is to be expected in the acid to be ozonized. This contaminant will be quantitatively volatilized as RuO_4 even though it is expected to have no deleterious effect on the organic removal process. Thus the off-gas treatment system should be designed accordingly.

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