

A MASS SPECTROMETRIC INVESTIGATION OF THE THERMAL OXIDATIVE REACTIVITY OF ETHYLENE GLYCOL

Paul W. BROWN, Walter J. ROSSITER Jr and Kevin G. GALUK

U.S. Department of Commerce, National Bureau of Standards, Gaithersburg, MD 20899, USA

Received 23 August 1985

The thermal oxidative stability of ethylene glycol was investigated over the temperature range of 100–126°C. Aqueous ethylene glycol solutions were heated in sealed tubes in the presence of metallic copper and without metal. Mass spectrometric analysis was used to determine the rates of O₂ consumption and CO₂ evolution during heating. Copper had a catalytic effect of the glycol degradation. It was found that the rate limiting step in the thermal oxidative process was not related to oxygen consumption, suggesting that the rate limiting step involved the formation of a free radical which subsequently reacts with O₂. The evolution of CO₂ continued to occur after total consumption of the O₂. This suggested that the CO₂ is evolved from one of the thermal oxidation products of ethylene glycol.

1. Introduction

Ethylene glycol based heat transfer liquids are commonly used in solar energy collection systems. As a consequence, the thermal and thermal oxidative stability of ethylene glycol is of importance since its acidic degradation products cause accelerated corrosion of metallic containment systems. Although little appears to have been reported in the literature regarding the thermal stability of ethylene glycol, it is generally accepted that heating aqueous ethylene glycol solutions in the presence of oxygen produces a thermal oxidative degradation [1,2]. In previous investigations [3–5] the thermal oxidative stability of ethylene glycol solutions in the range 75–100°C was assessed and the principal products were found to be oxalic, formic, and glycolic acids. These investigations have also shown that the formation of these degradation products in the absence of oxygen was negligible. In the present study the thermal oxidative stability of ethylene glycol at temperatures above the boiling point was investigated, since glycol-based heat transfer liquids are at times subjected to such temperatures in service.

2. Experimental

Heavy-walled glass tubes, having volumes of (60.0 ± 0.3) cc were fabricated. 10 cc volumes of 50/50 vol% vacuum distilled ethylene glycol/distilled water solutions were placed in the tubes. In some instances, copper coupons having surface areas of (15.0 ± 0.3) cm² were also placed in the tubes. The tubes were then sealed and

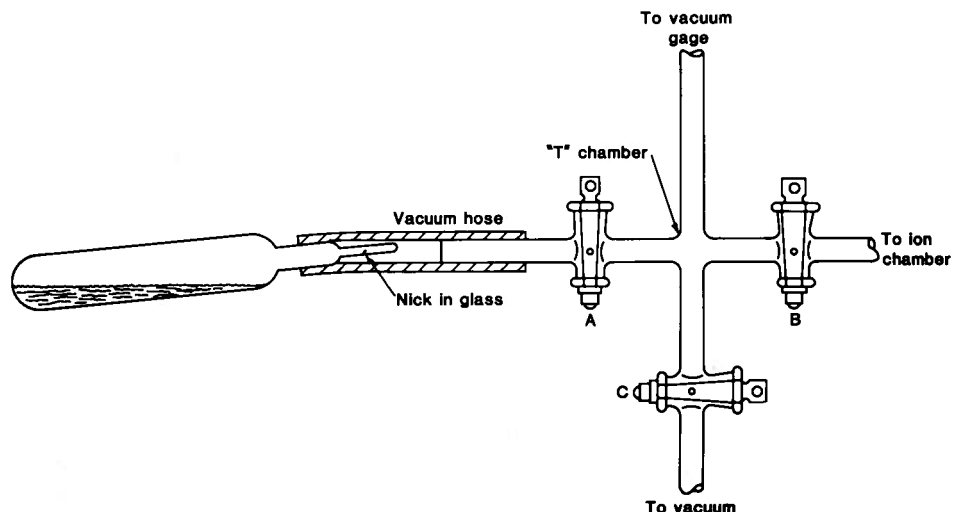


Fig. 1. Schematic of mass spectrometric sampling arrangement.

placed in forced air convection ovens where they were maintained at 100, 113 or $126 \pm 1^\circ\text{C}$. After predetermined lengths of time, the tubes were removed from the ovens and rapidly cooled by immersion in cold water. Mass spectrometric analyses for O_2 and CO_2 , and pH measurements were made on the degraded solutions. Prior to each mass spectrometric analysis, the ion chamber of the mass spectrometer was evacuated to 10^{-6} Torr and a scan taken to check the background. The system was then calibrated for O_2 and CO_2 and a correction factor determined. To analyze the composition of the atmosphere above the glycol solutions, the tubes were broken under vacuum as shown in fig. 1. After evacuation of the system, valves A, B and C were closed and the tip of the tube was fractured. A sample of the atmosphere in the tube was then bled into the T-chamber through valve A. Valve A was then closed and valve B to the ion chamber opened, allowing analysis. This procedure was repeated for replicate analyses of the atmosphere in the same tube.

pH measurements were carried out in the conventional manner using a glass electrode which had been calibrated over a range of pH which bracketed the measured values [3–5].

3. Results and discussion

Figs. 2 and 3 show the rates at which oxygen is consumed depending on the temperature and the presence of copper metal coupons in the system. The rate of oxygen consumption is more rapid in the presence of copper. If the rate limiting step were related to the consumption of oxygen, the rate law equation $-\text{d}[\text{O}_2]/\text{d}t = k[\text{O}_2]^n$ with $n =$ being nonzero would be expected. However, linear relationship between percent oxygen and time shown in figs. 2 and 3 indicates the consumption

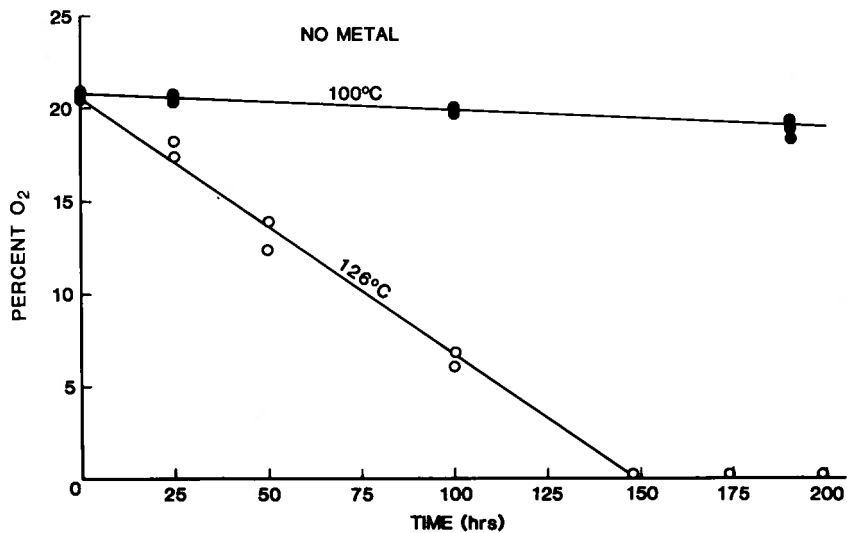


Fig. 2. Rates of oxygen consumption at 100 and 126°C in the absence of metal.

of oxygen to be zero order, $-d[O_2]/dt = k$. This implies that the rate limiting step for the thermal oxidative reaction under the present reaction conditions is not related to oxygen consumption. Rather, the rate limiting step may involve the

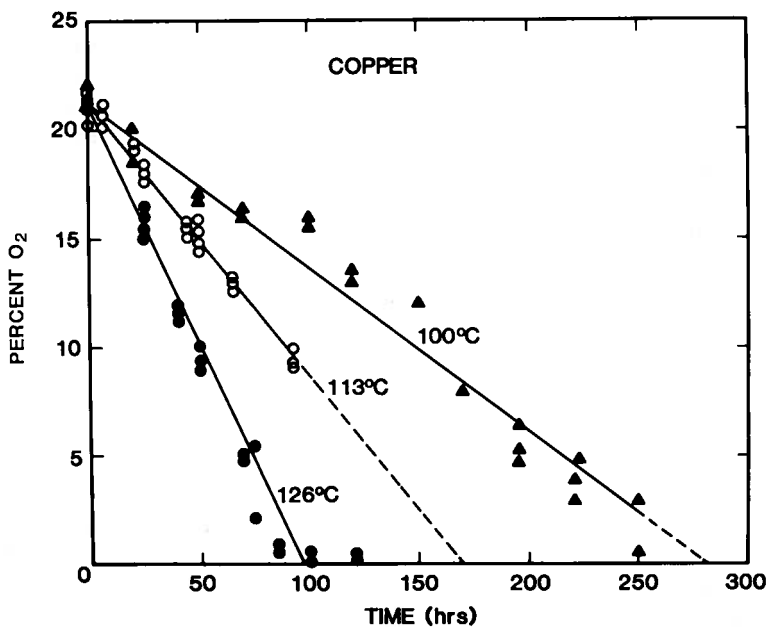


Fig. 3. Rates of oxygen consumption at 100, 113 and 126°C in the presence of copper.

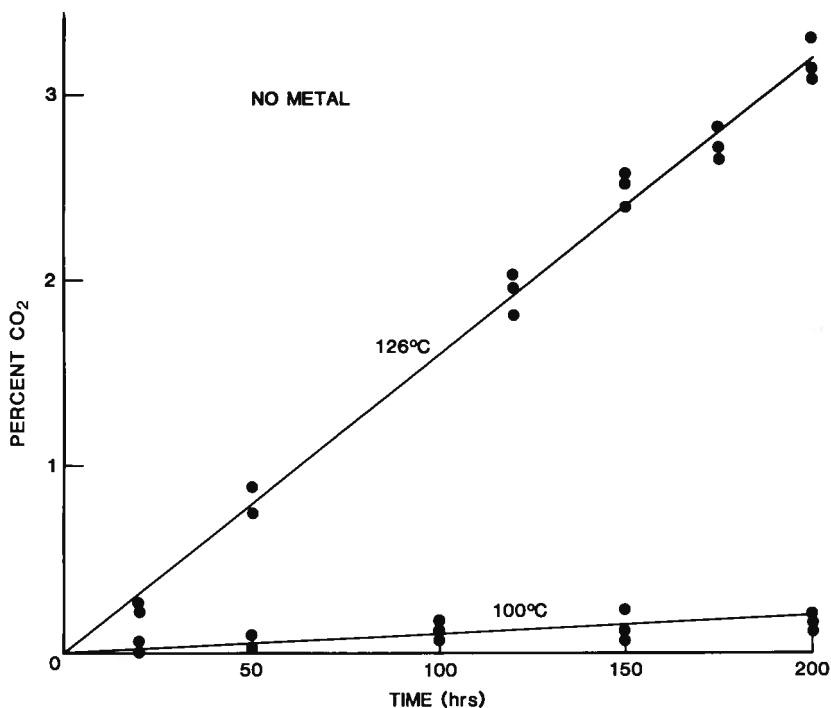


Fig. 4. Rates of CO₂ evolution at 100 and 126°C in the absence of metal.

formation of a free radical which then reacts with the oxygen in the system. A free radical mechanism has been observed in the thermal oxidation reaction of alcohols [6].

Based on the data in fig. 3 an Arrhenius activation energy of 12.4 kcal/mol for the consumption of oxygen in the presence of copper was calculated. Although the data presented in fig. 2 were insufficient to make a similar calculation to any degree of certainty, the activation energy for this process in the absence of copper appears to be higher. Taken together with the observation of accelerated formation of thermal oxidative ethylene glycol products at temperatures between 70 and 100°C in the presence of copper [1,3], a catalytic effect of copper on thermal oxidation of ethylene glycol degradation is suggested.

The results of this study have shown that CO₂ is a degradation product formed during the heating of aqueous glycol solutions in the presence of oxygen at temperatures as low as 100°C. Figs. 4 and 5 show the relative rates of CO₂ evolution depending on the temperature and the presence of copper. The evolution of CO₂ was observed at 100°C regardless of the presence of copper. However, with possible exception of the rates during the first 25 h, CO₂ evolution was more rapid in the systems containing copper metal. In all cases, the rates of CO₂ evolution increases with increasing temperature. Comparison of the data in figs. 2-5 for the rates of O₂ consumption and CO₂ evolution indicate the continued evolution of CO₂ even after

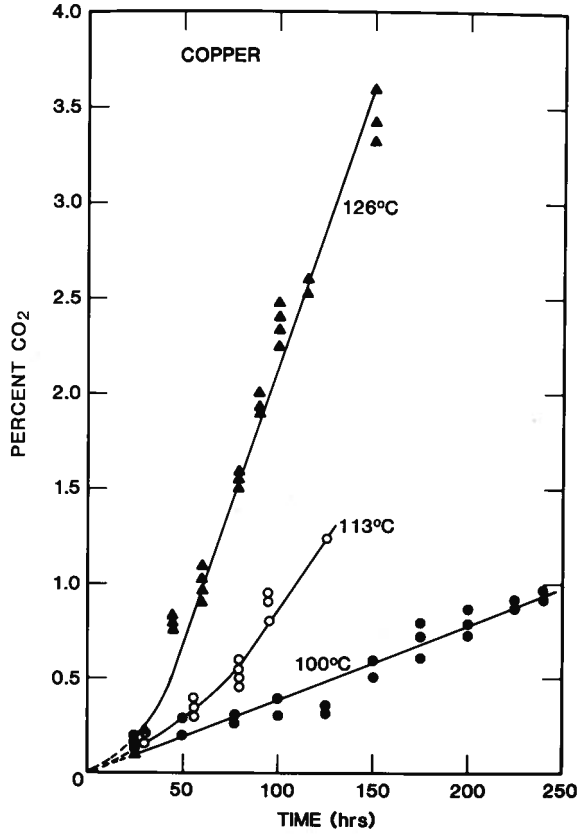


Fig. 5. Rates of CO₂ evolution at 100, 113 and 126°C in the presence of copper.

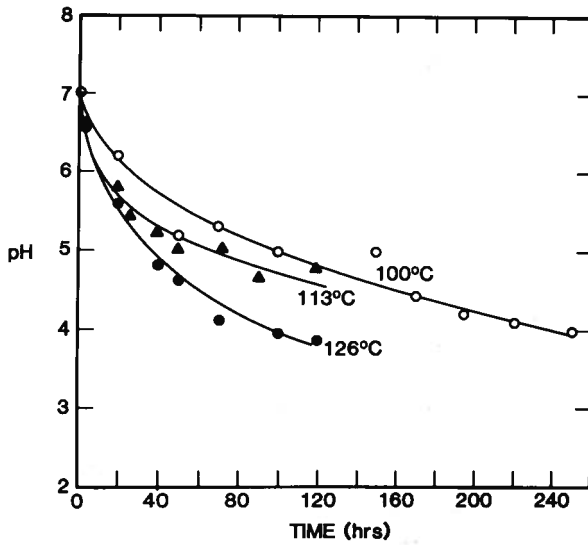


Fig. 6. Variations of solution pH at 100, 113 and 126°C in the presence of copper.

the oxygen in the tubes was exhausted. This observation suggests that CO_2 is evolved from one of the thermal oxidation products of ethylene glycol. For example, oxalic acid, which has previously been identified as a thermal oxidation product of ethylene glycol, is known to evolve CO_2 upon its thermal degradation at temperatures as low as 100°C [7].

The pH values of the solutions heated in the presence of copper are shown in fig. 6. The relative decrease in pH as a function of temperature is in accord with the relative rates of oxygen consumption. A pH value of 4 was reached after 100 h at 126°C , while 250 h of heating at 100°C were required to reach this same value. A previous investigation has shown, that under the condition of aeration, 2000 h of heating were required at 101°C to reach a similar value [5]. Whether this difference is related to the presence of CO_2 in the closed system is speculative.

4. Summary

The thermal oxidative degradation of ethylene glycol at temperatures as low as 100°C results in the evolution of CO_2 as one of the degradation products. The rate of O_2 consumption during this process appears to follow zero order kinetics. This implies that under the reaction conditions in the study the rate limiting step is independent of O_2 concentration and that a mechanism involving free radical initiation may be rate limiting. Both the rate of O_2 consumption and the rate of CO_2 evolution accelerated in the presence of copper.

Acknowledgement

The authors wish to acknowledge the U.S. Department of Energy, Office of Solar Heating Technologies for supporting this investigation. The assistance of Mr. Mike Manka, in conducting the mass spectrometry measurements is sincerely appreciated.

References

- [1] J.E. Clifford and R.B. Diegle, Review of State of the Art of Solar Collector Corrosion Processes, Battelle Columbus Laboratory Rept. No. DoE/CS/ 10510-T12 (1980).
- [2] J.G. Avery and J.J. Krall, Solar Eng. Contr. 1 (1982) 30, 34.
- [3] W. Rossiter, P. Brown and M. Godette, Solar Energy Mater. 9 (1983) 267.
- [4] W. Rossiter, M. Godette, P. Brown and K. Galuk, Solar Energy Mater. 11 (1985) 455.
- [5] J. Clifton, W. Rossiter and P. Brown, Solar Energy Mater. 12 (1985) 77.
- [6] E.T. Denisov, The Oxidation of Alcohols, Ketones, Ethers, Esters, and Acids in Solution, in: Chemical Kinetics, vol. 16, eds. C.H. Bamford and C.F.H. Tipper (1980).
- [7] A. Dinglinger and E. Schroer, Z. Physik. Chem. 179 (1937) 401.