Organic and Biological Chemistry

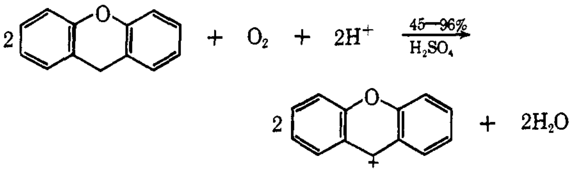
Acid Catalysis in O_2 Oxidations and the Possible Role of the Hydroperoxy Cation, HO_2^+

N. C. Deno, Edward L. Booker, Jr., Kenneth E. Kramer, and George Saines

*Contribution from the Department of Chemistry, Whitmore Laboratory,
The Pennsylvania State University, University Park, Pennsylvania 16802.*
Received March 15, 1969

Abstract: Xanthene reacts with O_2 in 45–96% H_2SO_4 to produce 2 mol of xanthyl cation/mol of O_2. The reaction is first order in xanthene and first order in H^+ activity. The existence of simple acid catalysis is interpreted as due to an interaction between H^+ and O_2 to form kinetically significant amounts of the hydroperoxy cation, HO_2^+.

Qualitative observations[1] had indicated that the oxidation of xanthene to xanthyl cation, eq 1, was due to oxygen from the air. The reaction was acid catalyzed, taking place instantly in 80% H_2SO_4, but very slowly in 45% H_2SO_4. A similar acid-catalyzed air oxidation has been observed on silica–alumina catalysts in the oxidation of triphenylmethane to triphenylmethyl cation,[2] eq 2. The stoichiometry in eq 2 is assigned by analogy with eq 1.



(1)

$$2(C_6H_5)_3CH + O_2 + 2H^+ \xrightarrow{SiO_2-Al_2O_3} 2(C_6H_5)_3C^+ + 2H_2O \qquad (2)$$

These reactions possess two points of interest. The first arises from the industrial importance of any type of selective oxidations of C–H bonds by air. Second is the catalysis of an O_2 oxidation by acid.

The evidence that O_2 was the oxidant came from three sources. First was the fact that a limiting concentration of xanthyl cation, 1.5×10^{-4} *M*, was produced in 83% H_2SO_4 as the initial xanthene concentration was varied from 10^{-6} to 10^{-3} *M*. This result is in accord with the concept that the amount of product is limited by a fixed supply of dissolved O_2. Second was the absence of any detectable SO_2, which would have been produced if H_2SO_4 were the oxidizing agent. Third is the qualitative fact (originally noted[1]) that stirring a solid suspension of xanthene in a closed system with 60–80% sulfuric acids failed to intensify the xanthyl cation color and failed to lead to dissolution of the xanthene.

Interpolation of a smoothed curve of data on the solubility of O_2 in sulfuric acids[3] gives a value of 0.62×10^{-4} *M* for 0.2 atm of O_2 in 83% H_2SO_4 after a small correction from 21 to 25°. The value 0.62×10^{-4} is about half the limiting value of xanthyl cation and means that 2 mol of xanthene are oxidized to xanthyl cation per mol of O_2 consumed, eq 1. Further evidence for this ratio is the failure to detect H_2O_2 (by starch and KI) in diluted reaction mixtures. A 1:1 ratio would presumably have left H_2O_2 as a reaction product.

The reaction rate was first order in xanthene concentration as shown by data in Table I. The reaction was also first order in H^+ activity as shown by the fit of the data to eq 3, Table II. It is probable that the rate is

$$-\mathrm{d}\log k = 0.85\mathrm{d}H_0 \qquad (3)^4$$

also first order in O_2 concentration though this was not directly tested.

Table I. Demonstration that the Rates for Reaction 1 are First Order in Xanthene in 65% H_2SO_4 at 25.0° [a]

Initial concn of xanthene, molarity $\times 10^6$	k sec$^{-1} \times 10^4$
1.96	5.4
3.93	5.3
7.86	5.2
19.6	5.4
39.3	5.5

[a] Rate constants were computed from the equation, $k = t^{-1}2.3 \log [(\text{xanthene})_0/(\text{xanthene})_t]$. No trend in values of k was discernible out to 90% completion. The data are exemplary. Similar results were obtained in 75 and 85% H_2SO_4. The O_2 was that due to saturation by air, estimated to be 0.62×10^{-4} *M* in 60 and 80% H_2SO_4 and 0.60×10^{-4} *M* in 70% H_2SO_4 from the data in ref 3. The O_2 is in large excess and the kinetics are pseudo first order in xanthene.

The over-all result in eq 1 and 2 is to abstract a hydride ion from the organic substrate. It is difficult to understand how protonation of xanthene or triphenylmethane could augment its hydride donating ability.

---

[1] N. Deno, G. Saines, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962).

[2] A. E. Hirschler and J. O. Hudson, *J. Catal.*, **3**, 239 (1964); A. E. Hirschler, *ibid.*, **5**, 390 (1966).

[3] A. Seidell and W. F. Linke, "Solubilities," 4th ed, Vol. 2, American Chemical Society, Washington, D. C., 1965, pp 1228–1230. The data of C. Bohr [*Z. Phys. Chem.*, **71**, 47 (1910)] were used primarily.

[4] For the definition and interpretation of the Hammett H_0 acidity function, see F. A. Long and M. Paul, *Chem. Rev.*, **57**, 15 (1957).

Table II. Effect of Acidity on the Rate of Oxidation of Xanthene by O_2

% H_2SO_4	H_0 (ref 4)	k_1,[a] sec^{-1}	Log k_1 + 6	Deviation in log k_1 from eq 3
45	−2.85	1.2×10^{-6}	0.079	0.00
55	−3.91	2.4×10^{-5}	1.38	0.00
65	−5.04	5.4×10^{-4}	2.73	0.05
71	−5.78	3.8×10^{-3}	3.58	0.00

[a] Values of k_1 were obtained as described in footnote *a* of Table I. Although the kinetics are probably first order in $[O_2]$, no correction was necessary since $[O_2]$, due to saturation by air, was 0.60×10^{-4} *M* (±5%) from 45 to 71% H_2SO_4.[3]

It is more attractive to attribute the acid catalysis to an interaction of O_2 with H^+. This would augment the electrophilic and hydride abstracting properties of O_2 because of the added positive charge. Unanswered is the question as to whether HO_2^+ is a singlet or triplet. The concentration of HO_2^+, though kinetically significant, must still be but a small fraction of the total O_2 concentration since the solubility of O_2 in 45–96% H_2SO_4 undergoes only minor variations.[3]

In eq 1, xanthene sustains a net loss of hydride, H^-, in forming xanthyl cation. This aspect is emphasized by the fact that only very good hydride donors, xanthene and 4,4′,4′′-trimethoxytriphenylmethane, undergo the acid-catalyzed oxidation by O_2.[1] Moderately good hydride donors (triphenylmethane, diphenylmethane, and 4,4′-dimethoxydiphenylmethane) are not oxidized by O_2 in 45–96% sulfuric acid.[5] Probably they would be oxidized if sulfonation did not intervene, and in fact, triphenylmethane is oxidized on alumina-silica surfaces.[2]

An oxidation of xanthene to xanthyl cation by O_2 has been observed in 2–30% aqueous perchloric acid.[6] The reaction is a free-radical reaction. It requires catalysis by Fe ions and shows a complex dependence on acidity.[6] The rate slowly increases from 2 to 17% $HClO_4$ and then decreases from 17 to 30% $HClO_4$. It is believed that this reaction bears no direct connection to the one reported herein.

Experimental Section

Titration for SO_2. The classic iodimetric method was used.[7] It is estimated that formation of 0.01 mol of SO_2 per mol of xanthene would have been detected.

Limiting Yield of Xanthyl Cation. Xanthene was introduced into 10 ml of 83% sulfuric acid (air saturated) by addition of 0–0.2 g of an acetic acid stock solution. Xanthyl cation formation was complete immediately. The acid mixture was diluted to 20% H_2SO_4 with O_2 free water and then further diluted with 20% H_2SO_4 until an absorbtivity of 0.2–1.0 (at 375 mμ, λ_{max} for xanthyl cation) was reached.

In principle, the absorbtivity of the reaction mixture could have been reduced by diluting with O_2-free 80% H_2SO_4 or by using 0.05-cm cells. Both of these procedures proved to be impractical. Alternate freezing and pumping failed to free completely the H_2SO_4 from O_2 and the solutions were too viscous to fill conveniently 0.05-cm cells.

It was particularly convenient to conduct the spectroscopic measurements in 20% H_2SO_4. The reaction was quenched so that protection from air was no longer required. At 20% H_2SO_4, the acidity is still high enough so that no significant fraction of the xanthyl cation is converted to 9-xanthenol.[8] The disproportionation of xanthyl cation to xanthene and xanthone is also slow enough so that there is no fading in the few minutes required for measurement.

Kinetic Studies. All experiments were conducted at 25.0° in closed systems. The xanthene was introduced by adding 0–0.2 g of an acetic acid stock solution to 10 ml of the requisite sulfuric acid. The xanthyl cation concentration was followed by the development of absorption at 375 mμ. The initial xanthene concentration was 10^{-5}–10^{-6} *M* so that O_2 was in excess and the reactions were pseudo first order.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

---

(5) 4,4′-Dimethoxydiphenylmethane was reported to be oxidized, but the appearance of 4,4′-dimethoxydiphenylmethyl cation was found to be due to traces of the carbinol present as an impurity.

(6) A. P. Ter Borg, H. R. Gersmann, and A. F. Bickel, *Rec. Trav. Chim.*, **85**, 899 (1966).

(7) W. S. Hendrixon, *J. Am. Chem. Soc.*, **47**, 1319 (1925); I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957, pp 449–462.

(8) The equilibrium is 1:1 in 11% H_2SO_4: N. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).