Rate Constants and Activation Energies for the Reactions of Triphenylmethyl and 9-Arylthioxanthyl Radicals with Dioxygen

Haijiang Wang and Vernon D. Parker*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA

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Triphenylmethyl radical reacts with dioxygen in dichloromethane with a second-order rate constant of $1.1 \times 10^7 \, dm^3 \, mol^{-1} \, s^{-1}$ at 298 K and an Arrhenius activation energy of $-4.1 \, kcal \, mol^{-1}$. 4-Phenyl-substituted thioxanthyl radicals are somewhat less reactive toward dioxygen in acetonitrile (second-order rate constants from 1.4×10^5 to $3.2 \times 10^5 \, dm^3 \, mol^{-1} \, s^{-1}$ at 298 K with Arrhenius activation energies of about $-3 \, kcal \, mol^{-1}$). A weak substituent effect ($\rho = -0.45$) was observed for the latter reaction series. The major products of these reactions are the corresponding carbonyl compounds, benzophenone and thioxanthone, believed to form by rearrangement after rate determining adduct formation between the radicals and dioxygen. The mechanism of adduct formation is believed to occur in two steps involving the formation of a complex in a pre-equilibrium followed by bond formation.

The reaction between free radicals and ground-state triplet dioxygen is expected to be a simple and nearly barrier-free reaction. Thus, even stabilized free radicals react rapidly with oxygen in low concentrations. In fact, we have previously observed[1] that triphenylmethyl radical ($Ph_3C^{\cdot}$) reacts with traces of dioxygen in dichloromethane at 208 K with a rate constant of about $5 \times 10^7 \, dm^3 \, mol^{-1} \, s^{-1}$. We anticipated a mechanism involving a radical–radical combination followed by irreversible product forming steps. However, our preliminary results on the study of the kinetics of the reactions of 9-arylthioxanthyl radicals with dioxygen included the surprising observation of negative apparent activation energies for these reactions.

Over the past several years, we have observed that many ion radical reactions are accompanied by apparent negative activation energies. These reactions include dimerization,[2,3] acid–base reactions,[4,5] and electrophile–nucleophile combinations.[6,7] Invariably, we have attributed these observations to two-step mechanisms involving first complex formation followed by bond-making or -breaking. These observations have supported the view that ion radicals are not expected to be very reactive. Negative activation energies have recently been observed in reactions of hydrogen atom[8] and alkyl radicals[9] in the gas phase and a general theoretical treatment of negative activation energies is available.[10]

Here we present further kinetic data on the reaction of triphenylmethyl radical with dioxygen in dichloromethane and examine the kinetics of the reactions of a variety of 4-substituted thioxanthyl radicals with dioxygen in acetonitrile. We find that these reactions all show similiar characteristics to the ion radical reactions mentioned above implicating a more complex mechanism than expected.

Results and discussion

The kinetic studies of the persistent radical–dioxygen reactions were carried out using the prepeak method.[11,12] The method is applicable to the study of rapid second-order reactions of electrode-generated intermediates with reactants in less than stoichiometric quantities. Kinetic prepeaks are observed only for rate-determining second-order reactions. The reader is referred to Ref. 12 for the details of mechanism analysis using this method. A typical voltammogram showing a prepeak along with the main peak is illustrated for the reaction of 9-phenylthioxanthyl with dioxygen in Fig. 1. 9-Phenylthioxanthylium ion $(5.0 \, mM)^{13}$ is reduced reversibly in acetonitrile–Bu_4NPF_6 (0.1 M) in an argon atmosphere and gives rise to a reversible cyclic voltammogram (Fig. 1a). In the presence of O_2, at concentrations insufficient to react with all of the free radicals generated in the forward scan, a prepeak is observed at a potential less negative than the main peak (Fig. 1b).

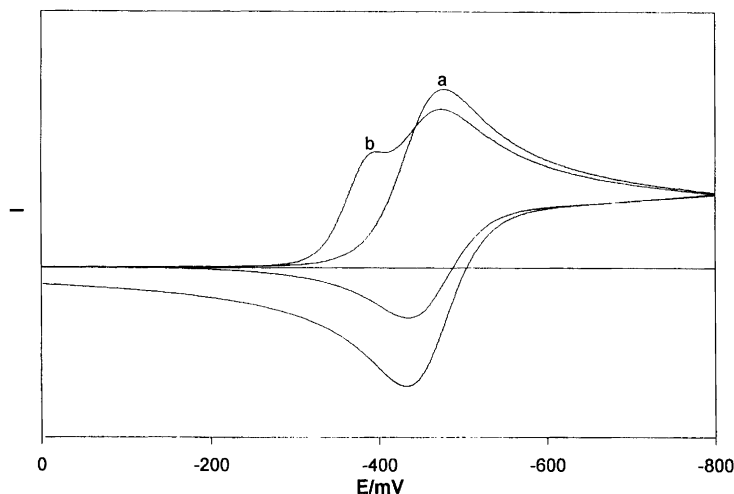* To whom correspondence should be addressed.

Fig. 1. Cyclic voltammograms for the reduction of 9-phenylthioxanthylium ion (5 mM) in acetonitrile–Bu$_4$NPF$_6$ (0.1 M) at a sweep rate of 100 mV s^{-1}: (a) under argon, (b) in the presence of O$_2$. The potential scale begins at 500 mV vs. an Ag$^+$/Ag reference electrode.

In order to assign rate contants it is necessary to know the concentrations of both substrate and dioxygen. We found it more convenient to determine [O$_2$] by the magnitude of the prepeak current than to prepare solutions of known concentration. Thus, the electrolyte solutions were first saturated with O$_2$ and then the concentration was adjusted to a convenient level for the analysis by purging with argon. The rate constant for the reaction of the radical with O$_2$ was then assigned by comparison with theoretical data obtained by digital simulation of charge transfer followed by an irreversible chemical step [eqns. (1) and (2)]. The second-order rate constants for the reactions between the thioxanthyl radicals and dioxygen are of borderline magnitude for observing prepeaks. Because of this it was necessary to use rather high substrate concentrations (5 mM) since at lower substrate concentrations, shoulders at the onset of the main peaks rather than prepeaks are observed.

$$R^+ + e^- \rightleftarrows R^\cdot \tag{1}$$

$$R^\cdot + O_2 \rightarrow \text{Products} \tag{2}$$

Our previous study of the reaction between Ph$_3$C$^\cdot$ and dioxygen in dichloromethane was carried out at a single temperature, 208 K. In order to compare the reactivity of the thioxanthyl radicals with that of Ph$_3$C$^\cdot$ toward dioxygen we determined rate constants for the latter reaction at temperatures ranging from -35 to $25\,^\circ$C (Table 1). The data give rise to an Arrhenius activation energy equal to -4.1 kcal mol^{-1} ($r^2 = 0.99$).

Second-order rate constants for the reactions of a series of 9-arylthioxanthyl radicals with dioxygen are listed in Table 2. The data give rise to a weak substituent effect [Hammett (σ_p) $\rho = -0.45$, $r^2 = 0.97$] showing a decrease in reactivity for electron-withdrawing substituents. The effects of temperature on the second-order rate constants for three of the radicals are summarized in

Table 1. The temperature dependence of the second-order rate constants for the reaction of triphenylmethyl radical with dioxygen.[a]

$T/^\circ$C	k/dm^3 mol^{-1} s^{-1}
-35	5.8×10^7
-20	3.5×10^7
-5	2.6×10^7
10	1.3×10^7
25	1.1×10^7

[a]Data obtained by prepeak measurements on voltammograms obtained during the reduction of triphenylmethyl ion (5 mM) in dichloromethane (0.1 M Bu$_4$NPF$_6$).

Table 2. Substituent effects on second-order rate constants for the reactions of 9-arylthioxanthyl radicals with dioxygen.[a]

p-Substituent	E_{rev}/mV[b]	k/dm^3 mol^{-1} s^{-1}
CH$_3$O	103	3.2×10^5
CH$_3$	118	2.8×10^5
H	131	2.4×10^5
Cl	162	1.9×10^5
CH$_3$CO	171	1.7×10^5
CF$_3$	184	1.4×10^5

[a]Prepeak measurements carried out on 9-arylthioxanthilium ions (5 mM) in acetonitrile (0.1 M Bu$_4$NPF$_6$) at 298 K. [b]Referred to NHE.

Table 3. Small negative (-3 kcal mol^{-1}) Arrhenius activation energies were observed for all three reactions.

The feature of the data in Tables 1–3 of most interest is the fact that negative Arrhenius activation energies are observed in all cases tested. This suggests that the mechanism of the free radical–dioxygen combination reaction is not the expected irreversible combination followed by product forming steps. The negative activation energies are more consistent with a pre-equilibrium association

Table 3. The temperature dependence of the second-order rate constants for the reactions of 9-arylthioxanthyl radicals with dioxygen.[a]

T/°C	$k/M^{-1}s^{-1}$		
	$X^b = CH_3O$	$X^b = H$	$X^b = CF_3$
−20	8.4×10^5	7.0×10^5	3.6×10^5
−5	5.9×10^5	4.4×10^5	2.5×10^5
10	4.1×10^5	3.9×10^5	1.7×10^5
25	3.2×10^5	2.4×10^5	1.4×10^5
E_a/kcal mol^{-1}	−3.3	−3.3	−3.2

[a]Prepeak measurements carried out on 9-arylthioxanthylium ions (5 mM) in acetonitrile (0.1 M Bu$_4$NPF$_6$). [b]p-Substituent on the 9-aryl group.

of the free radicals with dioxygen [eqn. (3)] followed by formation of a C–O bond at the 9-position of the free radicals [eqn. (4)].

$$R^{\cdot} + {}^{-}O{-}O^{\cdot} \rightleftarrows R^{\cdot}/{}^{-}O{-}O^{\cdot} \tag{3}$$

$$R^{\cdot}/{}^{-}O{-}O^{\cdot} \rightarrow R{-}O{-}O^{\cdot} \tag{4}$$

$$R{-}O{-}O^{\cdot} \rightarrow products \tag{5}$$

It is of interest to point out that the observation of negative activation energies for this series of reactions has precedence in the fact that negative activation energies are very commonly observed for various radical ion reactions.[2–7]

Experimental

Solvents and supporting electrolyte. Reagent grade acetonitrile and dichloromethane were distilled from phosphorus pentoxide and calcium chloride, respectively. Electrolyte solutions were prepared by dissolving tetrabutylammonium hexafluorophosphate, prepared by the reaction of tetrabutylammonium hydrogen sulfate with hexafluorophosphoric acid, in solvent and passing the solution through a column of active neutral alumina. The supporting electrolyte was recrystallized from dichloromethane–diethyl ether and dried under vacuum before use.

Reagents. Triphenylcarbenium hexafluorophosphate was used as received from Aldrich. 4-Substituted 9-arylthioxanthylium tetrafluoroborate salts were obtained by hydrolysis of the corresponding 9-arylthioxanthydrols in aqueous tetrafluoroboric acid solution. The 9-arylthioxanthydrols were prepared by the addition of the appropriate Grignard reagent to thioxanthen-9-one in diethyl ether. The 9-arylthioxanthinium salts were obtained by the action of HBF$_4$–O(C$_2$H$_5$)$_2$ on the corresponding hydrol. The products were washed with cold dry ether either followed by several washes with cold pentane. The purities of the salts were verified by ^{1}H NMR analysis.

Product analyses. The products of the electrolytic reduction of 9-phenylthioxanthinium ions in acetonitrile in the

presence of dioxygen were observed to be thioxanthen-9-one (85%) while benzophenone is the primary product[1] of the reaction of triphenylmethyl radical under the reaction conditions used in this study. The GC–MS yields of the carbonyl compounds were observed to be greater than 80% in all cases. The corresponding 9-arylthioxanthydrols were observed as minor products.

Kinetic measurements. Rate constants for the free radical–dioxygen reactions were carried out using the prepeak method.[11,12] Linear sweep voltammograms were recorded at a planar (0.8 mm diameter) platinum electrode using a PAR model 173D potentiostat driven by a Hewlett–Packard 3314A function generator. The analog signals were filtered using a Stanford Research System, Inc., model SR640 dual channel filter in the low pass mode. Data were recorded using a computer-interfaced Nicolet model 310 digital oscilloscope. The raw data were processed with a digital frequency domain filter. Peak potential and peak current data were extracted by carrying out a polynomial fit of the current–potential data in the region of the peaks on the voltammograms. Rate constants were assigned by comparison with theoretical data obtained by digital simulation.[13–16] The rate constants reported are the averages of at least nine replicate determinations. Dioxygen concentrations varied from about 2 to 5 mM.

Examples of the experimental data are illustrated in Table 4. In each case the voltammogram was first recorded and two quantities, the ratio (I_{ratio}) of current at the prepeak to that of the main peak and the difference in potential (ΔE^p) between the prepeak and the main

Table 4. Experimental prepeak data for the reaction of triphenylmethyl radical with dioxygen in dichloromethane (0.1 M Bu$_4$NPF$_6$).[a]

T/°C	$(I_{ratio})^b$	$(\Delta E^p)^c$	log(k/dm^3 mol^{-1} s^{-1})
−35	0.34	133.7	7.85
	0.49	127.6	7.81
	0.87	112.4	7.65
	0.83	114.4	7.70
−20	1.00	110.9	7.48
	0.94	114.2	7.54
	0.92	114.9	7.54
	0.92	114.6	7.54
−5	0.68	125.8	7.38
	0.72	126.2	7.43
	0.98	117.6	7.45
10	0.85	118.6	7.11
	0.85	118.8	7.11
	1.04	107.5	7.00
25	0.95	107.4	6.70
	0.75	119.6	6.81
	0.90	112.9	6.79

[a]Ph$_3$CPF$_6$ (5.0 mM), voltage sweep rate = 0.10 V s^{-1}. [b]The ratio of the current at the prepeak to that of the main peak. [c]The difference in electrode potentials between the prepeak and the main peak.

peak, were obtained by the data processing program. After the experimental data had been gathered digital simulation was carried out to obtain a theoretical voltammogram with the same values of I_{ratio} and ΔE^p as each of the experimental voltammograms. Each simulation required less than a minute and the average number of simulations needed to obtain a match between experimental and theoretical data was 4–5.

References

1. Bodner, G. S, Gladysz, J. A., Nielsen, M. F. and Parker, V. D. *J. Am. Chem. Soc. 109* (1987) 1757.
2. Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B 35* (1981) 341.
3. Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B 37* (1983) 379.
4. Parker, V. D. and Tilset, M. *J. Am. Chem. Soc. 108* (1986) 6371.
5. Reitstöen, B. and Parker, V. D. *J. Am. Chem. Soc. 112* (1990) 4968.
6. Reitstöen, B. and Parker, V. D. *J. Am. Chem. Soc. 113* (1991) 6954.
7. Xue, J.-Y. and Parker, V. D. *J. Org. Chem. 59* (1994) 6564.
8. Seakins, P. W. and Pilling, M. J. *J. Phys. Chem. 95* (1991) 9878.
9. Nicovich, J. M. and van Dijk, C. A. *J. Phys. Chem. 95* (1991) 9890.
10. Mozurkewich, M. and Benson, S. W. *J. Phys. Chem. 88* (1984) 6429.
11. Jensen, B. S. and Parker, V. D. *Electrochem. Acta 18* (1975) 665.
12. Parker, V. D., Zheng, G. and Wang, H. *Acta Chem. Scand. 49* (1995) 351.
13. Digital simulations were carried out using the Rudolph method[14-16] with a commercially available program (Digisim2 from Bioanalytical Systems Inc.)
14. Rudolph, M. *J. Electroanal. Chem. 314* (1991) 13.
15. Rudolph, M. *J. Electroanal. Chem. 338* (1992) 85.
16. Rudolph, M. In: Rubinstein, I., Ed., *Physical Chemistry: Principles, Methods and Applications*, Marcel Dekker, New York 1993.