

Steric hindrance effects on bimolecular coupling rate constants of carbon-centered radicals

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ABSTRACT: Carbon-centered radicals have historically been classified as either persistent or reactive in solution. Little attention has been given to finding a relationship between this reactivity and the steric hindrance of radicals. The bimolecular coupling rate constants of some aryl-substituted fluorenyl and xanthenyl radicals were determined utilizing fast-scan cyclic voltammetry and digital simulations. This rate constant was found to be attenuated from the diffusion-limited value as the twist of the aryl substituent increased; the twist was described by an appropriate dihedral angle (Θ). However, Θ was found to be insufficient to represent the steric shielding provided by the aryl groups. Instead, thickness parameters (Z) obtained from MOPAC RHF-PM3 calculations correlated well ($R^2 = 0.954$) with the coupling rate constants of the radicals considered. This parameter was taken as the greatest extent of the van der Waals surface in the area of the p-orbital holding the unpaired electron. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: radicals; bimolecular coupling; steric hindrance; anisotropy; kinetics; voltammetry

INTRODUCTION

As intermediates¹ in chemical reactions, free radicals are ubiquitous to organic chemistry and have been exploited in the synthesis of fine chemicals and economically important polymers.² Furthermore, reactions formerly classified as ionic are now thought to proceed by way of a radical intermediate involving single electron transfer (SET).³ In biochemistry, radicals are considered to play an important role in various enzyme reactions⁴ and have been implicated in the causes of several diseases.⁵ Knowledge of the kinetics of radical reactions is therefore requisite to understanding in these important areas.

Radicals possess an unpaired electron and should form a bond with another radical almost immediately. Coupling between neutral radicals is expected to occur at a diffusion limit where the rate constant is a function of the size of the molecule, the temperature and the viscosity of the solvent.⁶ However, in some cases the orbital containing the unpaired electron is sterically shielded by part of the molecule and is not accessible for bonding. These observations have sometimes led to over-generalization with many radicals classified^{7,8} as either reacting

at this diffusion limit or as persistent and virtually non-reactive.

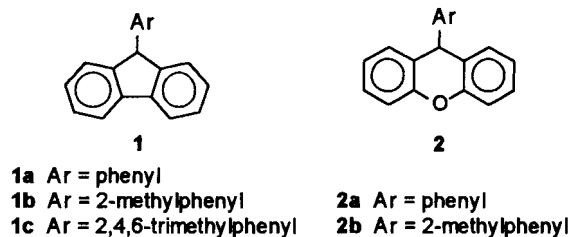
For example, nitroxide trapping agents, which are also radicals, were treated as reacting exclusively at the diffusion-controlled limit. However, it has now been recognized⁹ that structural features imparting steric hindrance will attenuate the reaction rate to the extent that the orbital containing the unpaired electron is blocked. Conversely, many carbon-centered radicals with large conjugated π systems were placed¹⁰ in a single category, persistent. However, our work finds that their bimolecular coupling rate constants differ by over seven orders of magnitude.

Copious studies have estimated the solution-phase thermodynamic stabilities of radicals in the form of bond dissociation energies (BDE).^{11–16} In most cases these values were based on cyclic voltammetric (CV) experiments. To facilitate the use of the available CV data, a diffusion-limited or totally persistent classification was applied.¹⁵ Radicals displaying chemical reversibility in the CV experiment were deemed persistent and their redox potential taken as equilibrium data. Radicals lacking chemical reversibility were assumed to react at the diffusion limit and an appropriate correction was applied.

We have observed¹⁶ that just as in the nitroxide trapping agents, the coupling rates of carbon-centered radicals show a range of values proportional to the extent of steric hindrance of the molecules. Two families of

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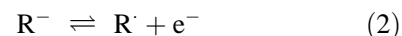
related molecules, aryl-substituted fluorenyl (**1**) and xanthenyl (**2**) radicals, were selected for this study.



EXPERIMENTAL

CV and fast-scan CV (FSCV) utilizing ultramicroelectrodes^{17–19} were combined with an implicit finite difference digital voltammetry simulation program²⁰ (DigiSim, v. 2.0, BioAnalytical Systems, West Lafayette, IN, USA) to yield rate constant data for these carbon-centered radicals. In the voltammetric experiments an appropriate carbon acid (R-H) in a tetra-*n*-butylammonium perchlorate electrolyte–dimethyl sulfoxide solvent solution (TBAP–DMSO) was treated under an inert atmosphere with a base (potassium dimsyl) to yield the corresponding anion (R[−]) [Eqn. (1)]. In the same solution, the anion was oxidized at a platinum disk electrode, producing the desired radical (R[•]) [Eqn. (2)]. The incipient radical was subsequently reduced [Eqn. (3)] back to the anion, as shown in Scheme 1.

This is an accepted protocol^{11–13} utilized in earlier experiments to determine the reduction potential of the radical–anion couple. In FSCV experiments the range of scan rates was selected¹⁷ to minimize edge diffusion, IR drop and double-layer charging effects for the size of the ultramicroelectrode (10, 25 and 100 μm diameter).



Scheme 1

If a radical lacked steric hindrance and the time-scale of the experiment was long, then a chemical reaction was observed. In previous work,¹⁶ the dependence of the current ratios (cathodic/anodic) on the concentrations of the radical precursor indicated this reaction was a bimolecular coupling [Eqn. (3)]. Also in that work, manipulation of the scan rate and observation of the current ratio were utilized to determine the coupling rate constants by means of a working curve.^{21,22} These values are listed in Table 1. Earlier publications^{8,23,24} indicate bimolecular products for this reaction. However, analysis was hampered by rapid conversion of the product to the corresponding peroxide. Gas chromatography–mass spectrometry (GC–MS) following oxidative electrolysis at a platinum grid electrode of the 9-phenylfluorenyl anion in TBAP–DMSO showed significant amounts of the bimolecular product (*m/z* 483) and the dissociated peroxide (*m/z* 257). Observation of a current ratio dependence upon concentration and reaction product analysis suggested that a bimolecular coupling was the only plausible mechanism.

In a refinement from the working curve approach, digital simulations (DigiSim, BioAnalytical Systems) were used to determine the coupling rate constants. When possible, voltammograms were taken at scan rates yielding current ratios <1 (chemical irreversibility) to current ratios of 1 (reversibility). Given the appropriate experimental parameters, including an expected rate

Table 1. Bimolecular coupling rate constant as a function of dihedral angle (θ) and steric thickness (Z)

Compound	Dihedral angle, ^{a,b} θ (°)	Thickness, ^{b,d} Z (Å)	Bimolecular coupling rate constant ^e (log l mol ^{−1} s ^{−1})	Electron transfer rate constant ^{e,h} (cm s ^{−1})
1a	42.2	3.32	7.70 7.15 ^{f,g}	0.48
1b	55.1	5.63	4.00 3.92 ^{f,g}	0.44
1c	74.5	7.35	0.85	
2a	66.5 ^c	4.69	4.48 4.56 ^{f,g}	0.51
2b	77.6	6.15	1.90	0.32

^a Defined in Fig. 1.

^b Calculated using the PM3 parameter set of MOPAC.

^c Comparable to values obtained by ESR spectroscopy. In Ref. 32 the dihedral angle is 70–80°, in Ref. 33 63° and in Ref. 34 60°.

^d Defined in Fig. 3.

^e Determined by fitting a digital simulation to a fast scan cyclic voltammogram. Log of the estimated⁶ diffusion-limited rate constant (l mol^{−1} s^{−1}) in DMSO is 8.90.

^f Determined by application of a working curve^{21,22} to current ratios at various scan rates.

^g Data previously published in a dissertation.¹⁶

^h Determined by application of a working curve³⁵ to shift of peak potential at various scan rates. The value for oxidation of ferrocene was found to be 0.82 cm s^{−1} (at a Pt working electrode¹⁹ in TBAP–acetonitrile 0.95).

Table 2. Experimental parameters used in digital simulations of voltammograms

Parameter	Approximate electrode diameter (μm)		
	10	25	100
Scan rate range (V s^{-1}) ^a	500–50000	50–500	5–50
Temperature (K)	298	298	298
Uncompensated resistance (Ω) ^b	5.5×10^5	4.0×10^5	5.0×10^4
Double-layer capacitance (F) ^b	2.0×10^{-11}	2.0×10^{-10}	3.0×10^{-9}
Electrode area (cm^2) ^b	9.0×10^{-7}	8.0×10^{-6}	4.0×10^{-5}
α	0.5	0.5	0.5
k_s (cm s^{-1}) ^b	0.4	0.4	0.4
K_{eq}^c	100000	100000	100000
k_b^c	0.1	0.1	0.1
Diffusion coefficient of anion ($\text{cm}^2 \text{s}^{-1}$) ^b	3.0×10^{-6}	3.0×10^{-6}	3.0×10^{-6}
Diffusion coefficient of radical ($\text{cm}^2 \text{s}^{-1}$) ^b	3.0×10^{-6}	3.0×10^{-6}	3.0×10^{-6}
Diffusion coefficient of dimer ($\text{cm}^2 \text{s}^{-1}$) ^b	3.0×10^{-6}	3.0×10^{-6}	3.0×10^{-6}

^a Limits selected to minimize edge diffusion, IR drop and charging current effects.¹⁷

^b Derived from experiments with ferrocene in TBAP–DMSO solution.

^c Coupling reaction was assumed to be essentially irreversible.²¹

constant of the coupling reaction, the digital simulation program produced voltammograms matching those of the experiment. The experimental parameters used in these simulations are listed in Table 2 and were measured in experiments with ferrocene in the TBAP–DMSO solution. As expected, uncompensated resistance and double-layer capacitance, while minimized, were dependent on the size of the electrode and were included in the model parameters. The coupling rate constants derived from this fitting process were then correlated with the steric hindrances of the corresponding radicals.

The steric hindrance of the radical was estimated by means of the optimized geometry obtained from restricted Hartree–Fock (RHF) level MOPAC v. 5.0 calculations²⁵ using the PM3²⁶ Hamiltonian with the configuration interaction (CI) specified by the DOUBLET keyword. Self-consistent field molecular orbital (SCF-MO) semiempirical methods have been used to determine the energies and geometries of many free radicals.²⁷

Reagents

Tetra-*n*-butylammonium perchlorate (TBAP) (TCI, Portland, OR, USA, >98%) was recrystallized three times from 10% hexane (Fisher Scientific, Pittsburgh, PA, USA, >98.5%)–ethyl acetate (Fisher, >99.9%) and dried in a vacuum oven (50 °C) until used. Dimethyl sulfoxide (DMSO) (Aldrich, Milwaukee, WI, USA, 98%) was distilled under vacuum from sodium amide (Aldrich, 90%) and stored under an argon atmosphere.²⁸ Potassium dimethyl sulfoxide was produced by reaction of freshly distilled DMSO with potassium hydride (Aldrich, 35 wt% in mineral oil) in a filter under argon.²⁸ The material was shielded from light and stored in a freezer until used.

9-Phenylfluorene (Aldrich, 99%) was used as supplied. 9-(2-Methylphenyl)fluorene,²⁹ 9-(2,4,6-trimethyl-

phenyl)fluorene,²⁹ 9-phenylxanthene²⁸ and 9-(2-methylphenyl)xanthene³⁰ were synthesized by Grignard reaction of the appropriate aryl bromide [bromobenzene (Aldrich, 99%), 2-bromotoluene (Aldrich, 99%) or 2-bromostyrene (Aldrich, 99%)] and an aromatic cyclic ketone [9-fluorenone (Aldrich, 98%) or 9-xanthene (Aldrich, 99%)] followed by reduction of the alcohol with a mixture of iodine, acetic acid and hypophosphorous acid.²⁹ Mass spectra and melting-points^{28–30} confirmed the identities of the products. All manipulations of solutions were done by syringe (Series 1000, Hamilton, Reno, NV, USA) under argon passed through an oxygen trap (RGP 125-R1, Labclear, Oakland, CA, USA) and a gas drying unit (26800, Drierite, Xenia, OH, USA).

Apparatus

Platinum disk microelectrodes (1.6 mm diameter) were used as supplied (MF-2013, BioAnalytical Systems). Platinum ultramicroelectrodes (10, 25 or 100 μm diameter) were either purchased (MF-2005, MF-2150, BioAnalytical Systems) or fabricated by sealing the appropriate sized wire (Goodfellow, Berwyn, PA, USA, 99.9%) in soft glass followed by polishing. The voltammetric cell consisted of a four-necked round-bottomed flask (25 ml) fitted with a platinum wire auxiliary electrode (0.5 mm diameter, Aldrich, 99.9%), an O-ring adapter for sealing to the microelectrode or ultramicroelectrode, a fritted chamber to provide a salt bridge communicating with a silver (0.5 mm diameter wire, Aldrich, 99.9%)/silver iodide reference electrode (saturated tetra-*n*-butylammonium iodide, Aldrich, >99%) in TBAP–DMSO and a three-way stopcock to provide connection to a vacuum/argon manifold for insertion of a sample syringe. The temperature of the cell was maintained at 25 °C.

CV experiments with microelectrodes utilized a general-purpose electrochemical workstation (BAS 100 B/W, BioAnalytical Systems). To accommodate the ultramicroelectrodes of the FSCV instrument, a current-to-voltage converter was fabricated making use of a low-bias current operation amplifier (AD 549JH, Analog Devices, Norwood, MA, USA). The remainder of the instrument consisted of a custom-fabricated potentiostat, a 100 MHz digital function generator (2416A, Pragmatic, San Diego, CA, USA) and a quad 200 MHz digital oscilloscope (9304A, LeCroy, Chestnut Ridge, NY, USA). The potentiostat, cell and current-to-voltage converter were housed inside a Faraday cage. The signal generator and oscilloscope were connected by means of a GPIB bus to a personal computer and the experiment was controlled and data collected by a virtual instrument program written in a data acquisition language (LabVIEW, v. 3.0.1, National Instruments, Austin, TX, USA).

RESULTS

The aryl-substituted fluorenyl and xanthenyl radicals studied have large planar fused-ring systems surrounding the p-orbital holding the unpaired electron. The chemically anisotropic character³¹ of these reactants dictates that only a trajectory more or less orthogonal to the plane could result in a successful coupling. Additionally, the path is limited by the steric bulk of the aryl group (Ar). Note that for all of the molecules considered the rate constant was less than the estimated diffusion-limited value of $8.90 \log 1 \text{ mol}^{-1} \text{ s}^{-1}$. Therefore, restrictions on the trajectory due to the large planar ring system and the aryl substituent prevent any of these molecules from realizing a diffusion-limited rate.

Since these molecules have the fused-ring system in common, differences in steric hindrance must be attributed to the bulk of the aryl group. The extent of this hindrance was initially estimated by the appropriate dihedral angle (θ) between the aryl group and the ring system. Repulsions between the H-1 and H-8 hydrogens of the fused-ring system and the *ortho*-hydrogens of the aryl group cause the ring to twist, eclipsing the p-orbital holding the unpaired electron, making it less available for bonding and thereby attenuating the rate. With methyl substitution of the *ortho* positions of the aryl group the ring twists even more. In Fig. 1, θ is shown at the plane described by atoms α , 9 and 1' and the plane containing 9, 1' and 2' where α and 9 are in the fused-ring system (**1** or **2**) and 1' and 2' are in the aryl group (**a**, **b** or **c**).

The relationship between the coupling rate constant and θ is shown in Table 1. It can be seen that as θ increased from 25.3 to 74.5° the rate constant decreased from 7.70 to 0.85 $\log 1 \text{ mol}^{-1} \text{ s}^{-1}$. The effect was the same for fluorenyl and xanthenyl radicals. However, scatter of the data points when both families of radicals were plotted revealed that θ was not an adequate measure

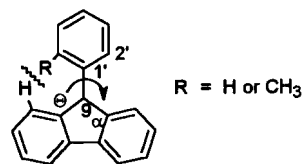


Figure 1. Dihedral angle (θ) as a measure of relative steric hindrance of an aryl substituent

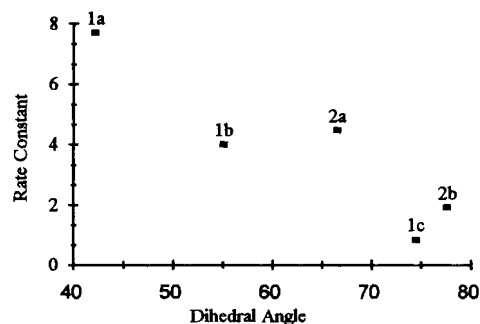


Figure 2. Coupling rate constant as a function of dihedral angle (θ)

of differences in the steric effect (Fig. 2). The magnitude of θ did not reflect differences in the inherent steric bulk of the aryl ring due to the 2-methyl (2-methylphenyl, Ar = **b**) or the 2-methyl and 6-methyl substituents (2,4,6-trimethylphenyl, Ar = **c**).

Considering this limitation, it seemed that the coupling rate constant would be better correlated to a parameter that directly measures the hindrance due to the twisted aryl group. A thickness parameter (Z) was determined by projecting the aryl group and any substituents on a plane longitudinally bisecting the p-orbital containing the unpaired electron as illustrated in Fig. 3. Attached methyl substituents were permitted to rotate to their lowest energy conformation and the thicknesses included the greatest extent of the van der Waals (VDW) surface.

The correlated values of Z are listed with the appropriate reaction rate constants in Table 1. A significant advantage of using Z rather than the dihedral angle is that the steric hindrance of many different substituent groups may be compared. The linear relationship of the coupling rate constant to Z for aryl-substituted fluorenyl and xanthenyl radicals is shown in Fig. 4.

Using either the dihedral angle or thickness to predict the reaction rate constant assumes an early transition state

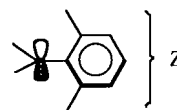


Figure 3. Steric thickness (Z , VDW distance) in the plane of the unpaired electron p-orbital

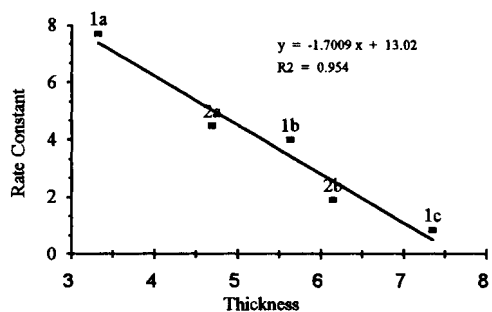


Figure 4. Correlation of coupling rate constant with steric thickness (Z)

in the bimolecular coupling. If the reaction proceeds by way of a late transition state then the steric strain in the product would be a better correlate of the rate constant. However, steric strain in the product would follow similar trends to the dihedral angle or the thickness since all depend on the nature of the aryl substituent.

CONCLUSIONS

For the radicals studied, accessibility of the orbital holding the unpaired electron is the determining factor for the rate of bimolecular coupling. This correlation of coupling rate constant of organic radicals to steric hindrance had not been elucidated to this extent in previous studies. Further investigations using the FSCV-digital simulation method of analysis will expand this correlation to include other families of radicals.

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