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A New and Convenient Method for Radical Anion Lifetime Determination

John H. Penn* and Elizabeth D. Cox

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

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A new method for the determination of radical anion lifetimes has been developed. This technique utilizes the diminished reactivity of a radical ion as a function of the concentration of an added electron acceptor in order to determine quenching parameters which may be used to obtain the lifetime. This technique is similar to a photochemical method for the determination of triplet excited-state lifetimes. The key step to developing this technique is the elimination of highly absorbing charge-transfer complexes in the solution. The kinetic analysis for determining the radical anion lifetimes is reported as well as the lifetimes of several radical anions determined by this technique.

Reactive intermediates are now an essential part of modern chemistry. The reactions of these intermediates may be divergent and go through several different pathways to form products. This has been demonstrated in the chemistry of carbenes,[1] where hydrogen atom abstraction as well as insertion may be observed under various conditions. Studies in our laboratory have been concerned with radical anion intermediates and their subsequent reaction pathways leading to product formation. In order to study these reaction pathways, a method for determining the lifetime of the radical anion was needed. In this fashion, we would be able to probe the effect of different chemical reagents on potential reaction pathways.

Previous methods for determining radical ion lifetimes have their own characteristic limitations. The usual electrochemical techniques such as cyclic voltametry[2] or a potential-controlled rectangular pulse technique[3] fail when the lifetimes are less than 0.1 ms. Time-resolved laser spectroscopic techniques for the monitoring of intermediates having short lifetimes are well-known but are expensive and available in only a few laboratories.[4] Saveant has developed a homogeneous redox catalysis method for determining radical anion lifetimes in the nanosecond to microsecond range.[5] However, electrochemical techniques often rely on the high ionic strengths of their solvents to conduct the current. Therefore, the solvent conditions employed for electrochemical techniques may be dramatically different than those incurred under normal reaction conditions. Thus, we desired a technique which was both inexpensive and would allow the determination of lifetimes under less severe solvent conditions.

Our approach to this problem involves a novel extension of a known photochemical lifetime technique. Cristol has developed a technique for excited-state triplet lifetime determinations in which the quantum yield for product formation is plotted against the quencher concentration when using a constant ratio of quencher to reactant.[6] The excited-state triplet lifetime is determined from the slope of this plot by assuming that triplet excited-state quenching occurs at a diffusion-controlled rate. This technique requires a reactive triplet excited state. Excited-state quenching by transfer of excited-state energy to a compound containing a lower energy triplet excited state diminishes the relative amount of reaction. We reasoned that electron transfer occurring by diffusion control should be similar to excited-state energy transfer. Thus, if electron-transfer quenching occurs analogously to excited-state quenching, the lifetime of the radical anion would be available by observing the amount of reaction vs. the concentration of an appropriate electron acceptor.

Scheme I. Kinetic Analysis Used for Radical Anion Lifetime Determinations

$$S \xrightarrow{h\nu} S^*$$

$$S^* \xrightarrow{k_d} S$$

$$S^* + D \xrightarrow{k_{et1}} S^{\bullet -} + D^{\bullet +}$$

$$S^* + A \xrightarrow{k_q} S + A$$

$$S^{\bullet -} \xrightarrow{k_r} P$$

$$S^{\bullet -} \xrightarrow{k_{ds}} S$$

$$S^{\bullet -} + A \xrightarrow{k_{et2}} S + A^{\bullet -}$$

Our kinetic analysis is shown in Scheme I. The substrate is excited to yield a singlet or a triplet excited state (S^*) which is capable of decay (k_d) directly to the ground state or of radical anion formation through interaction with an electron donor (k_{et1}). The radical anion ($S^{\bullet -}$) is capable of reacting to form product (k_r) or decaying to starting substrate (k_{ds}). An electron acceptor in the solution adds two more reaction pathways to the analysis. The excited state may be quenched to its ground state (k_q) or the radical anion may transfer an electron to the acceptor (k_{et2}). If the radical anion transfers an electron to the acceptor, no reaction will occur. Thus, a decrease in the relative amount of reaction is expected as the concentration of electron acceptor is increased.

This is shown quantitatively by the following equations. The quantum yield for product formation may be viewed as the product of several probabilities as shown in eq 1.

$$\Phi = P_{RIF}P_P \qquad (1)$$

Thus, the quantum yield for product formation (Φ) is given by the probability of radical ion formation (P_{RIF}) multiplied by the probability of product formation by the radical ion (P_P). In the absence of an electron acceptor, the

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(1) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368.

(2) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980.

(3) Mueller, J.; Kersten, D.; Heckner, K. N. *Z. Phys. Chem.* **1972**, *258*, 666.

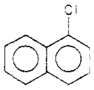
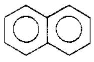
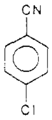
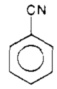
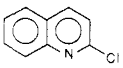
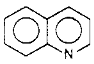
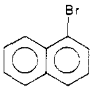
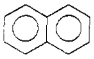
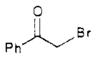
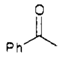
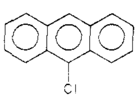
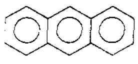
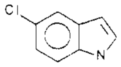
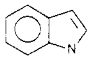
(4) (a) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (b) Barik, R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 4309. (c) Zimmt, M. B.; Doubleday, C., Jr.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724. (d) Szwarc, M. *Pure Appl. Chem.* **1979**, *51*, 1049.

(5) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Saveant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

(6) (a) Cristol, S. J.; Daughenbaugh, R. J.; Opitz, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 6347. (b) Ilenda, C. S.; Daughenbaugh, R. J. Cristol, S. J. *Mol. Photochem.* **1976**, *7*, 281.

0022-3263/86/1951-4447$01.50/0

Table I. Radical Anion Lifetime Data

parent compound	product	electron donor[d]	electron acceptor[d]	slope[c]	decay rate[c]	lit. value	ref
		DMHD	NB	580	5.0×10^7	5×10^7	*a*
		TMP	NB	970	3.0×10^7		
		DMHD	DNB	580	5.0×10^7		
		DMHD	NB	580	5.0×10^7	5×10^6 5×10^8	*b* *a*
		DMHD	NB	29000	1.0×10^6	6×10^5	*a*
		DMHD	NB	73	4.0×10^8	3×10^8	*a*
		DMHD	NB	29000	$<1.0 \times 10^6$	6×10^3	*b*
		TMP	NB	29000	$<1.0 \times 10^6$	1×10^2	*a*
		DMHD	NB	2900	1.0×10^7		

[a] Reference 3. [b] Reference 11. [c] Results are accurate to ±20%. [d] DMHD, 2,5-dimethyl-2,4-hexadiene; TMP, tetramethylpiperidine; NB, nitrobenzene; DNB, 1,3-dinitrobenzene.

quantum yield is given by eq 2, while the quantum yield in the presence of acceptor is given by eq 3.

$$\Phi_0 = \left[\frac{k_{\mathrm{et1}}[\mathrm{D}]}{k_{\mathrm{d}} + k_{\mathrm{et1}}[\mathrm{D}]}\right] \times \left[\frac{k_{\mathrm{r}}}{k_{\mathrm{r}} + k_{\mathrm{ds}}}\right] \tag{2}$$

$$\Phi = \left[\frac{k_{\mathrm{et1}}[\mathrm{D}]}{k_{\mathrm{d}} + k_{\mathrm{et1}}[\mathrm{D}] + k_{\mathrm{q}}[\mathrm{A}]}\right] \times \left[\frac{k_{\mathrm{r}}}{k_{\mathrm{r}} + k_{\mathrm{ds}} + k_{\mathrm{et2}}[\mathrm{A}]}\right] \tag{3}$$

Thus, the ratio of the quantum yields, Φ_0/Φ is given by eq 4.

$$\frac{\Phi_0}{\Phi} = \left[1 + \frac{k_{\mathrm{q}}[\mathrm{A}]}{k_{\mathrm{d}} + k_{\mathrm{et1}}[\mathrm{D}]}\right] \times \left[1 + \frac{k_{\mathrm{et2}}[\mathrm{A}]}{k_{\mathrm{r}} + k_{\mathrm{ds}}}\right] \tag{4}$$

While this equation initially appears formidable, several simplifications are available experimentally. The first is to make $k_{\mathrm{et1}}[\mathrm{D}] \gg k_{\mathrm{d}}$. The physical significance of this condition is that all excited states are decaying via the radical anion. By choosing an electron donor with a sufficiently low ionization potential and by using a high concentration of the electron donor, electron transfer will occur on every collision of an excited-state molecule with the electron donor. By keeping $[\mathrm{A}]/[\mathrm{D}]$ constant and $\ll 1$, the first term of eq 4 reduces to 1 since the maximum possible rate of k_{q} is the diffusion-controlled rate. Thus, eq 4 reduces to the form shown in eq 5. Graphical treatment of the relative product yields as a function of the electron-acceptor concentration gives a plot which has a slope of $k_{\mathrm{et2}}/(k_{\mathrm{r}} + k_{\mathrm{ds}})$. Assuming that k_{et2} is diffusion-controlled, the total decay rate of the radical anion ($k_{\mathrm{r}} + k_{\mathrm{ds}}$) is available. The lifetime of the radical anion is obtainable from eq 6.

$$\frac{\Phi_0}{\Phi} = 1 + \left[\frac{k_{\mathrm{et2}}[\mathrm{A}]}{(k_{\mathrm{r}} + k_{\mathrm{ds}})}\right] \tag{5}$$

$$\tau = 1/(k_{\mathrm{r}} + k_{\mathrm{ds}}) \tag{6}$$

The high concentration of electron donor also has another advantage. If $k_{\mathrm{et1}}[\mathrm{D}] \gg k_{\mathrm{d}}$, then any excited state will decay by way of the radical anion. Thus, if direct excitation results in the formation of product, this pathway for formation of product will be unimportant in the kinetic analysis.

This method requires only two assumptions. First, the rate of electron-transfer quenching in solution is assumed to be equal to the rate of diffusion. This has been found experimentally to be true if there is a sufficient difference in ΔG for electron transfer.[7] Second, the transfer of an electron to the excited-state chromophore is followed by dissociation into ions. Although the probability of dissociation into ions may not be unity, a constant probability will affect Φ_0 and Φ by the same amount and will not change the experimental results.

The critical experimental problem in this research was to find an electron donor and an electron acceptor which did not have a charge-transfer absorption band in the region of interest. Traditional electron donors such as triethylamine or aniline were found to give strong charge-transfer absorptions with electron acceptors such as nitrobenzene. Irradiation of these complexes would be expected to yield ions other than those expected from the kinetic analysis shown in Scheme I and would thus render the approach invalid. However, it was found that neither 2,5-dimethyl-2,4-hexadiene nor 2,2,5,5-tetramethylpiperidine formed such absorbing complexes with electron acceptors such as nitrobenzene or 1,3-dinitrobenzene. It should be noted that the choice of donors and acceptors is extremely important since it is necessary to maintain $k_{\mathrm{et1}} = k_{\mathrm{et2}} = k_{\mathrm{diff}}$. Preliminary experiments using maleic anhydride as an electron acceptor yielded spurious results.

Thus, using this technique, we have determined the lifetimes of a number of haloaromatics as shown in Table I. Numerical values for the slope were not included in

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[7] Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 6858.

this table unless the correlation coefficient from a linear least-squares analysis exceeded 0.95. Combining the slope with the known value[8] of 2.9×10^{10} M^{-1} s^{-1} for the rate of diffusion in acetonitrile, lifetime data are available. In all cases where literature data are available, our method yields results that are in satisfactory agreement with previously reported values.

In order to show that the technique is general and not compound specific, we have utilized different electron donors and electron acceptors. The lifetime of the 1-chloronaphthalene radical anion is the same whether 2,5-dimethyl-2,4-hexadiene or 2,2,5,5-tetramethylpiperidine is used as the electron donor. Similarly, the same lifetime for the 1-chloronaphthalene radical anion within experimental error is obtained when either nitrobenzene or 1,3-dinitrobenzene was used as the electron acceptor.

A further test of the method relates to triplet excited-state initiation of the chemical reactions. The well-known heavy atom effect enhances triplet excited-state formation and causes a diminished singlet excited-state lifetime. Thus, it is more difficult to intercept all singlets with an electron donor before the triplet excited state is formed. Since the triplet excited state has a lower energy, diffusion-controlled electron transfer may not be achieved. However, as long as the triplet excited state has a sufficient electrophilicity (as defined by the Rehm–Weller equation[9]), ion formation may still be assumed to be facile. As shown in Table I, the lifetime obtained for 1-bromonaphthalene (BN) is in good agreement with Savaent's data, even though the singlet excited-state lifetime of BN is only 75 ps.[10] Since the diffusion rate[8] for acetonitrile is 2.9×10^{10} M^{-1} s^{-1} and the decay rate of the singlet excited state is 1.3×10^{10} M^{-1} s^{-1}, a significant fraction of the excited-state electron-transfer quenching arises through the triplet excited state.

We have examined other compounds for which radical anion lifetime data have been reported. In all cases, the lifetimes determined by our technique are in reasonable agreement with literature values. In order to provide a test of the technique, we have also measured lifetimes for compounds for which no information is available. It should be noted that a practical limitation of this method places a lower bound on the total decay rate of the radical ion measurable at 1×10^6 s^{-1} (upper bound on the lifetimes measurable of 1 μs). This limitation arises because acceptor concentrations of 10^{-5} M are necessary for accurate measurements of longer lifetime components. Trace amounts of oxygen or other impurities may serve to quench the reaction at similar concentrations.

It should be noted that the other species (e.g., ion pairs of the radical anion and the radical cation of the electron donor or charge-transfer complexes involving the radical anion) may be involved along the reaction coordinate. In this work, the perturbation of the lifetime due to the environment of the radical anion must be small. The lifetime of the radical anion of 1-chloronaphthalene is similar, even though two different electron donors of quite different structure were used in the lifetime determinations. Additionally, the agreement of our data with the data obtained by Savaent,[5] using a diffusional technique incorporating 4-methoxybenzophenone or anthracene as catalysts, justifies our choice of the term "radical anion" in this work. In general, standard mechanistic criteria (e.g., use of different electron donors, different lifetime techniques) must be used to firmly establish the identity of the reactive intermediate in question.

In summary, we believe that our results have demonstrated a new and convenient method for the determination of radical anion lifetimes. The method follows a known photochemical technique and shows the promise of adopting other photochemical techniques to the study of reactive intermediates.

Experimental Section

Liquid chemicals used in this research were freshly distilled before usage. Acetonitrile was distilled from calcium hydride. All solid chemicals were used as received from Aldrich. Solutions were degassed with purified nitrogen for 15 min prior to irradiation and then sealed with latex septa. Irradiations were performed in a Southern New England Ultraviolet Rayonet (RPR-100) photochemical reactor on a merry-go-round apparatus to ensure that each sample received an identical amount of light. Product yields were determined by GLC and were kept to less than 50% conversion to minimize secondary photoreactions or light absorption by products. Graphical treatment of the data yielded Stern–Volmer constants. Data were not incorporated into Table I unless the correlation coefficient of a least-squares analysis was greater than 0.95.

Separation of reaction mixtures was performed on a Hewlett-Packard 5890A GC equipped with a 10-m phenylmethylsilicone Megabore column. Quantitative analyses of these reaction mixtures were obtained on a Hewlett-Packard 3390A reporting integrator and were measured relative to the area of hexyl cyanide used as an internal standard. UV spectra were obtained on a Varian DMS-100 spectrophotometer.

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Registry No. p-ClC_6H_4CN radical anion, 68271-91-0; $PhCOCH_2Br$ radical anion, 104576-67-2; 2-chloroquinoline radical anion, 34528-55-7; 9-chloroanthracene radical anion, 74430-88-9; 5-chloroindole radical anion, 104576-68-3; 1-chloronaphthalene radical anion, 51703-40-3; 1-bromonaphthalene radical anion, 51703-42-5.

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(8) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(9) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(10) Hilinski, E. F.; Huppert, D.; Kelly, D. F.; Milton, S. U.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 1951.

(11) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103.