## Tracer Diffusion Coefficients of Naphthalene, **Biphenyl**, and Anthracene

## Sır:

A previous study reported the utility of tracer diffusion coefficients of aromatic molecules in solutions of interest to organic electrochemists.<sup>1</sup> Herein we report the tracer diffusion coefficients  $(D_{tr})$  of naphthalene, biphenyl, and anthracene in the solvent systems: 75% dioxane-25% water (D-W), dimethylformamide (DMF), and acetonitrile (MeCN). All solvents contained 0.1 M tetraethylammonium perchlorate supporting electrolyte. The organic molecules and solvents were chosen to provide maximum correlation with electrochemically determined D values in the literature. Secondly, these solvent systems provide a good test of the constancy of the product of D times viscosity  $(D\eta).$ 

The experimental techniques were identical with those described previously.<sup>1</sup> The organic molecules were labeled generally by the method of Yavorsky and Gorin.<sup>2</sup> The viscosities of the solvents with supporting electrolyte and electroactive species present were measured at 25° with an Ostwald viscometer.

## **Results and Discussion**

Table I summarizes the measurements. As the next to the last column shows, the product of  $D_{\rm tr}$  times viscosity  $(D\eta)_{tr}$  for each of the three molecules is clearly a given compound by a factor of two or more with only one value (anthracene in MeCN) within the experimental deviation of the tracer data. These figures first attest to the reliability of the  $D_{\rm tr}$  values (the product  $D\eta$  should be constant) and, secondly, indicate that almost all of the electrochemically determined D values for these compounds are surely incorrect. The  $D_{\rm el}$  values determined in the present study were obtained from the appropriate diffusion current constants using the Ilkovic equation for a dropping mercury electrode. To evaluate the diffusion constant, the diffusion current  $(i_d)$  was taken as the difference between the observed  $i_d$  and the residual current. The value of  $m^{2/3}t^{1/6}$  was determined at the applied potential at which  $i_d$  was measured. All values of  $D_{el}$  from the literature were calculated directly from stated diffusion constants or from listed  $i_d$  values combined with  $m^{2/3}t^{1/6}$  data measured at the applied potential as mentioned above.

The large errors in  $D_{el}$  arise, of course, in the false assumption that one can assign with certainty the value  $n_{\rm T}$ , the total number of electrons transferred in the electrochemical reaction. In DMF and MeCN it is normally assumed  $n_{\rm T}$  = 1 and for dioxane-water  $n_{\rm T}$  = 2. While electron paramagnetic resonance studies indicate without question that the anion radicals of naphthalene, biphenyl, and anthracene are the predominant products during reduction in DMF and MeCN, the polarographic currents do not correspond

Table I. Comparison of Tracer and Electrochemical Diffusion Coefficients<sup>a</sup>

Compound	Solvent	$D_{\rm tr} \times 10^5$ , cm. <sup>2</sup> /sec.	$D_{\rm e1} \times 10^5$ , cm. <sup>2</sup> /sec.	Viscosity, mp.	$D\eta \times 10^{5}$	
					$(D\eta)_{\rm tr}$	$(D\eta)_{e1}^{b}$
Naphthalene	D-W	0.56	0.62 (3) 0.62 (6)	18.80	10.5	11.7 11.7
	DMF	1.27	2.5 2.9 (9)	8.55	10.8	21.4 24.8
	MeCN	2.74	6.9	3.88	10.6	26.8
Biphenyl	D–W DMF	0.57 1.20	1.26 (3) 1.41	18.80 8.66	10.7 10.4	23.8 12.2
	MeCN	2.48	9.4	3.92	9.7	36.8
Anthracene	D–W	0.52	0.39 (3) 0.31 (4)	18.80	9.8	7.3 5.8
	DMF	1.19	1.32 (9) 0.78 (7)∘	8.55	10.2	11.3 6.7
	MeCN	2.55	2.65 $(5)$ 6.6 $(8)^d$	3.92	10.0	10.4 25.8

<sup>a</sup> The number in parentheses to the right of  $D_{e1}$  refers to the literature source of the diffusion current constant from which  $D_{e1}$  was calculated, assuming  $n_T = 1$  for DMF and MeCN and  $n_T = 2$  for D-W.  $D_{e1}$  values without reference numbers were determined in this study <sup>b</sup> The  $(D\eta)_{tr}$  values were calculated from the viscosity measured in this study and given in column 5. There is a small error involved since some of the Del values were measured with different supporting electrolytes and have viscosities slightly different from those of the literature electrochemical studies. • Measured by alternating current polarography. • Measured by anodic oxidation at a platinum electrode via chronopotentiometry.

a constant within experimental error. On the other hand, using electrochemical D values determined in this study and from the literature,  $^{3-9}$   $(D\eta)_{el}$  varies for

- (1) T. A. Miller, B. Lamb, K. Prater, J. K. Lee, and R. N. Adams' Anal. Chem., 36, 418 (1964).
  - (2) P. M. Yavorsky and E. Gorin, J. Am. Chem. Soc., 84, 1071 (1962).
    (3) H. A. Laitinen and S. Wawzonek, *ibid.*, 64, 1765, 2365 (1942).
- (4) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, Rec. trav. chim., 73, 355 (1954).
- (5) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, J. Electrochem. Soc., 102, 235 (1955).
- (6) G. J. Hoijtink and J. van Schooten, Rec. trav. chim., 71, 1089 (1952). (7) A. C. Aten, Thesis, University of Amsterdam, 1959.

to integral one-electron transfers. These measured currents are the sum of the one-electron process plus contributions from the presence of proton donors in these solvents and background processes. It is noteworthy that biphenyl and naphthalene, which are more difficult to reduce than anthracene (and whose polarographic waves are therefore closer to background reduction), show serious differences in  $D_{el}$  and  $D_{tr}$ .

- (8) J. Voorhies and N. H. Furman, Anal. Chem., 31, 381 (1959),
- (9) A. C. Aten, C. Büthker, and G. J. Hoijtink, Trans. Faraday Soc., 55, 324 (1959).

The corresponding values for anthracene are in much better accord. (The anthracene  $D_{\rm el}$  value of 6.6  $\times$ 10<sup>-5</sup> cm.<sup>2</sup>/sec. in MeCN is based on anodic oxidation and clearly is a case of incorrect assignment of  $n_{\rm T}$ .) Small differences between  $D_{tr}$  and  $D_{el}$  as shown in Table I for naphthalene in D-W, and biphenyl and anthracene in DMF, may well be explained by overlap of the inherent inaccuracies of the two methods. We believe the probable error in the  $D_{\rm tr}$  values is ca.  $\pm 5\%$ and about  $\pm 2\%$  in the viscosities. The probable errors in  $(D\eta)_{tr}$  are then about  $\pm 7\%$  although the data given appear to be fortuitiously less than these limits. The unmodified Ilkovic equation was used in all polarographic calculations. Further, very rapid drop times are encountered at the high negative reduction potentials of these compounds. Diffusion current measurements under these conditions are subject to considerable error. In addition there may be smaller error contributions from differences in supporting electrolytes and purity of the solvents used in the various polarographic studies.

It is difficult to access the errors in the  $D_{\rm el}$  value of  $0.78 \times 10^{-5}$  cm.<sup>2</sup>/sec. for anthracene obtained by alternating current polarography.<sup>7</sup> Although Aten indicates an uncertainty of  $\pm 2\%$  in this *D* value, the value of  $1.32 \times 10^{-5}$  cm.<sup>2</sup>/sec. determined by d.c. polarography<sup>9</sup> is in agreement with  $D_{\rm tr}$  in the sense discussed above.

The importance of the present work lies not only in establishing what appears to be a reliable set of  $D_{\rm tr}$ values for several hydrocarbons (from which approximate *D* values in other solvents can be obtained via the  $D\eta$  relationship) but also in its implications in the study of electrode processes. Especially for organic substances reduced or oxidized near background potentials, this study emphasizes that limiting currents may give false impressions of  $n_{\rm T}$ . Electrode mechanisms originating with  $n_{\rm T}$  calculations should be strongly supported by independent information.

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## Paramagnetic Intermediates in the Condensation of Nitrosobenzene and Phenylhydroxylamine<sup>1</sup>

Sir:

Reaction of nitrosobenzene (0.005 *M*) and phenylhydroxylamine (0.005 *M*) in the presence of 0.05 *M* potassium *t*-butoxide in deoxygenated dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution at 23 ± 1° produces essentially a quantitative yield of nitroso-

(1) Reactions of Resonance Stabilized Anions. XVI. Work supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds. benzene radical anions<sup>2</sup> in <0.5 sec. In this solvent

$$C_{6}H_{5}NO + C_{6}H_{5}NHOH \xrightarrow{B^{-}} 2C_{6}H_{5}NO$$

the radical anion decays slowly over a period of days.

In the absence of added base in dimethyl sulfoxide, *t*-butyl alcohol, ethanol, or benzene the reaction of nitrosobenzene (0.005 *M*) and phenylhydroxylamine (0.005 *M*) gives rise to low concentrations ( $\sim 10^{-4}$  *M*) of phenyl nitroxide (C<sub>6</sub>H<sub>5</sub>NHO·),<sup>3</sup> detected and identified by the e.s.r. spectrum shown in Figure 1, that persist for a period of hours, even in the presence of oxygen. Presumably the phenyl nitroxide is slowly formed and slowly destroyed. After the e.s.r. signal has decayed an essentially quantitative yield of azoxybenzene can be isolated.

In ethanol containing sodium hydroxide, nitrosobenzene and phenylhydroxylamine rapidly react to yield up to 96% of azoxybenzene. Nitrosobenzene radical anions can be detected and identified under flow conditions<sup>2</sup> but rapidly decay when the flow is stopped. Figure 2 illustrates a stopped flow experiment of a solution 0.005 *M* in nitrosobenzene, 0.005 *M* in phenylhydroxylamine, and 0.05 *M* in sodium hydroxide after mixing.<sup>4</sup> The maximum concentration of nitrosobenzene radical anion detected (~0.005 *M*) occurred at the fastest flow rate, which represented a flow time of 0.5 sec. between mixing and detection. Under flow conditions the mixed solution underwent a blue to green to yellow color transformation in a matter of seconds.

The decay curve for nitrosobenzene radical anions given in Figure 2 follows second-order kinetics from a nitrosobenzene radical anion concentration of 0.005 to 0.0001 M with an empirical rate constant of 1.40  $\times$ 10<sup>2</sup> l./mole-sec. The kinetic and e.s.r. results suggest the following rapid equilibrium in the condensation reaction occurring in basic solution.<sup>5</sup>

$$2C_{6}H_{5}NO^{-} \xrightarrow{K_{N}} C_{6}H_{5}N \xrightarrow{N}C_{6}H_{5} \xrightarrow{} C_{6}H_{5}N \xrightarrow{N}NC_{6}H_{5} \xrightarrow{} C_{6}H_{5}N \xrightarrow{N}NC_{6}H_{5} \xrightarrow{} C_{6}H_{5}N \xrightarrow{} NC_{6}H_{5} \xrightarrow{} C_{6}H_{5} \xrightarrow{} C_{6} \xrightarrow{} C_{6}H_{5} \xrightarrow{} C_{6} \xrightarrow{} C_$$

(2) The e.s.r. spectrum is similar to that reported previously [F. J. Smentowski, J. Am. Chem. Soc., 85, 3036 (1963)]. The nitrosobenzene radical anion has restricted rotation around the bond between the aromatic ring and the nitrogen atom leading to magnetically nonequivalent o-hydrogen atoms. The situation is complicated by the fortutious magnetic equivalence of one o-hydrogen atom and the p-hydrogen atom. The same behavior has been noted in the azobenzene radical anion (results of Dr. R. Konaka). For nitrosobenzene radical anion the h.f.s.c. are  $a^{N} = 10.10$ ,  $a_{c_{1}}^{H} = 4.02$ ,  $a_{p}^{H} = 4.02$ ,  $a_{c_{2}}^{H} = 3.65$ , and  $a_{m}^{H} = 1.29$  (ethanol. 23°).

the first, c. are  $a^{n} = 10.10$ ,  $a_{o_1}^{n} = 4.02$ ,  $a_{p}^{-1} = 4.02$ ,  $a_{o_2}^{n} = 5.03$ , and  $a_m^{H} = 1.29$  (ethanol, 23°). (3) A. L. Buchachenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1120 (1963); C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, 230 (1964).

(4) Nitrosobenzene in basic ethanol solutions produces a significant but low steady-state concentration of nitrosobenzene radical anion<sup>2</sup> that persists for minutes. In the presence of oxygen these solutions yield nitrobenzene while in the absence of oxygen azoxybenzene is produced [e.g., E. Bamberger, Ber., 35, 732 (1902)]. That the rapid formation of azoxybenzene described herein is not connected with this latter process is illustrated by the observation that, under the reaction conditions, nitrosobenzene and aniline condense to form azobenzene contaminated by no more than a trace of azoxybenzene [results of Dr. F. J. Smentowski]. Phenylhydroxylamine in basic solution does not give an e.s.r. signal in the absence of oxygen. In the presence of traces of oxygen the nitrosobenzene radical anion can be detected. Oxidation on a synthetic scale yields a mixture of nitrobenzene and azoxybenzene.

(5) In ether or tetrahydrofuran solution, *p*-nitrosotoluene or *p*-nitrosodiomethylaniline react with sodium to produce p-RC<sub>6</sub>H<sub>4</sub>NO<sup>-</sup> Na<sup>+</sup>,