

ELECTRON EXCHANGE BETWEEN ANTHRACENE ANIONS AND PYRENE MOLECULES IN SOLUTION*

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The rate of a homogeneous electron transfer reaction between a neutral molecule and its radical anion has been measured for a number of aromatic hydrocarbons.¹⁻⁵ The rate of electron exchange between different aromatic hydrocarbons (heterogeneous electron transfer) has not previously been measured by e.s.r. techniques. Arai *et al.*⁶ have measured rate constants k for heterogeneous electron transfer reactions in isopropanol by pulse radiolysis studies. Analysis of their experimental results depends on the equilibrium position being favoured very much in one direction. For those molecules with similar electron affinities, it is possible to measure the rate of heterogeneous electron transfer by e.s.r. line broadening. We have estimated the rate constant for heterogeneous electron transfer between anthracene anions and pyrene molecules by this method.

An approximately 10⁻³M solution of anthracene dianions was prepared in 1,2-dimethoxyethane (DME) by potassium reduction.⁷ Neutral anthracene (A) or pyrene (P) was added to convert the dianions into monoanions. Weighed quantities of neutral pyrene were then added through breakseals. The following reactions occurred.



When pyrene was added in step (1), the broadened e.s.r. spectrum was a superposition of the spectra of anthracene and pyrene monoanions. The electronic absorption spectrum of the solution also showed the presence of both anions. On

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¹ Ward, R. L., and Weissman, S. I., *J. Am. chem. Soc.*, 1954, **76**, 3612; 1957, **79**, 2086.

² Layloff, T., Miller, T., Adams, R. N., Fah, H., Horsfield, A., and Proctor, W., *Nature*, 1965, **205**, 382.

³ Jones, M. T., and Weissman, S. I., *J. Am. chem. Soc.*, 1962, **84**, 4269.

⁴ Bruning, W. H., and Weissman, S. I., *J. Am. chem. Soc.*, 1966, **88**, 373.

⁵ Malinoski, G. L., and Bruning, W. H., *J. Am. chem. Soc.*, 1967, **89**, 5063.

⁶ Arai, S., Grev, D. A., Dorfman, L. M., *J. chem. Phys.*, 1967, **46**, 2572.

⁷ Paul, D. E., Lipkin, D., and Weissman, S. I., *J. Am. chem. Soc.*, 1956, **78**, 116.

addition of a large excess of neutral pyrene, the pyrene anion spectrum is extensively broadened because of homogeneous electron exchange (4).

At 2.69 gauss from the middle line, the intensity of the anthracene anion peak is estimated to be at least four times that of the neighbouring pyrene anion peak. Hence, to a first approximation, increase in width of this line may be considered to be caused by broadening of the anthracene anion lines by exchange reactions (2) and (3). The rate constant for reaction (3) in DME was measured separately as $(7.3 \pm 1.0) \times 10^8$ l. mole⁻¹ sec⁻¹. This is to be compared with the value of $(1.2 \pm 0.1) \times 10^9$ and $(4.8 \pm 1) \times 10^8$ l. mole⁻¹ sec⁻¹ in dimethylformamide.^{2,8} The broadening due to exchange reaction (3) was estimated in each case and subtracted from the total line broadening.

A correction was necessary to account for the decrease in intensity of the anthracene anion peak caused by reaction (2). This was done by comparing the line width after the addition of pyrene with the width of an equally intense line obtained by diluting the original solution before the addition of pyrene.

TABLE 1

RATE OF ELECTRON EXCHANGE BETWEEN ANTHRACENE ANIONS AND PYRENE MOLECULES

Concn. of (excess) pyrene added (M)	0.8×10^{-3}	2.0×10^{-3}	6.0×10^{-3}	7.5×10^{-3}
Line-width increase (gauss)	0.009	0.046	0.037	0.066
k (l. mole ⁻¹ sec ⁻¹)	1.7×10^8	3.5×10^8	1.0×10^8	1.4×10^8

TABLE 2

RATE CONSTANTS FOR ELECTRON TRANSFER REACTIONS

System	k (l. mole ⁻¹ sec ⁻¹)
Benzene-benzene anion ⁴	$7.7 \pm 0.8 \times 10^7$
Naphthalene-naphthalene anion ¹	$7.6 \pm 3 \times 10^7$
Anthracene-anthracene anion ⁶	$1.2 \pm 0.1 \times 10^9$
Pyrene-anthracene anion	$1.9 \pm 1.0 \times 10^8$

The rate constant k_1 for electron exchange between anthracene anions and pyrene molecules was estimated using the method described by Ward and Weissman.¹ Since the broadening of the hyperfine lines is small compared with the separation between lines, the rate of electron exchange is given by

$$\frac{\delta H_p}{\delta H_0} = \frac{k_1[P]}{\delta H_0 2.83 \times 10^6 \pi \sqrt{3}} \quad (5)$$

δH_0 is the width of the line after the first addition of pyrene or anthracene, δH_p is the increase in line width on adding excess pyrene, and $[P]$ is the concentration of excess pyrene added. The results obtained are given in Table 1. The value of k was $1.9 \pm 1.0 \times 10^8$ l. mole⁻¹ sec⁻¹. In Table 2, the rate constants for homogeneous

⁸ Hirota, N., Ph.D. Thesis, Washington University, St. Louis, Mo., 1963, pp. 107-8.

electron transfer reactions are compared with the heterogeneous rate constant estimated here. Our value is larger than the rate constant for either benzene-benzene anion or naphthalene-naphthalene anion exchange. This might be explained by a higher surface charge density on the smaller aromatic anions, and hence a greater solvent-anion interaction.

Since aromatic free-radical anions yield spectra with a total spread of *c.* 10^8 c/s and individual line widths of 10^5 – 10^6 c/s, this method would be limited to exchange reactions which occur at the rate of 10^4 to 10^9 times per second. Thus the method should prove useful in the determination of other heterogeneous electron transfer rates between hydrocarbons of similar electron affinity.

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