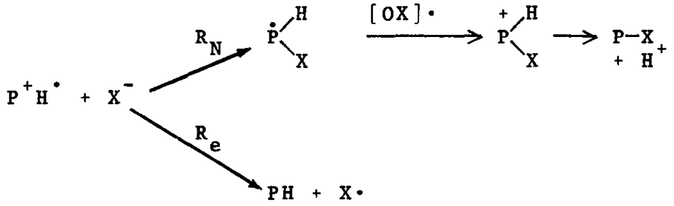
Tetrahedron Letters No. 36, pp 3103 - 3106, 1977. Pergamon Press. Printed in Great Britain.

THE REDUCTION OF PERYLENE RADICAL CATION BY NUCLEOPHILIC ADDITION

Ted R. Evans* and L. F. Hurysz
Research Laboratories, Eastman Kodak Co., Rochester, N. Y., 14650
(Received in USA 13 May 1977; received in UK for publication 14 July 1977)

The reactivity patterns of radical cations with nucleophiles present apparent anomalies as recently discussed by Eberson.[1] Of the two reactions observed with perylene radical cation, nucleophilic addition or reduction, the halides iodide, bromide, and chloride lead only to reduction while cyanide and nitrite add to the radical cation. The apparent anomaly lies in the fact that both cyanide and nitrite are more easily oxidized than is chloride. In order to rationalize this behavior, Eberson has postulated a symmetry forbiddenness for the nucleophilic reaction between the halides and perylene radical cation.



In contradiction to Eberson's postulate, Rozhkov et al.[2] have presented evidence that fluoride ion can react nucleophilically with radical cations.

We have examined the rates of reaction of perylene radical cation with various nucleophiles and arrive at conclusions contrary to those expressed by Eberson.[1]

Perylene radical cation was prepared by biphotonic photoionization[3] in either methanol or acetonitrile, and the rates given in Table 1 are those derived by measuring the disappearance of the radical cation at 540 nm in the presence of the given nucleophiles. All rate constants given are the result of two or more experiments at different concentration of nucleophiles.

The rate constants for electron-transfer reactions can be related to the oxidation potentials of the electron donors by the Marcus theory.[4,5] Any attempt to fit the data given in Table 1 to the expected shape, Figure 1, for the relative rates for the iodide, bromide, and chloride reactions with perylene radical cation indicates that either bromide is reacting slower than expected or chloride is reacting much faster than expected. The important point is that since bromide and chloride differ in oxidation potential by at least 0.27 V,[1,6,7] their reactivities, unless they react at the diffusion-limited rate, should differ by several orders of magnitude.

TABLE 1

Second-Order Rate Constants for the Reaction with Perylene Radical Cation and Oxidation Potentials and Nucleophilic Constants for the Nucleophiles

	Nucleophile	Solvent	Rate Constant M^{-1} Sec^{-1}	$E^{a}_{1/2}$	n^{b}
1.	I^-	CH_3OH	4.7×10^{9}		7.42
		CH_3CN	2.1×10^{10}	0.2	
2.	CHS^-	CH_3OH	2.1×10^{5}		6.7
		CH_3CN	1.6×10^{6}		
3.	CN^-	CH_3OH	4.6×10^{5}		6.7
		CH_3CN		0.7	
4.	Br^-	CH_3OH	9.1×10^{4}		5.79
		CH_3CN	1.0×10^{6}	0.4	
5.	Cl^-	CH_3OH	6.9×10^{4}		4.37
		CH_3CN	6.3×10^{5}	0.8	
6.	$CH_3CO_2^-$	CH_3OH	7.5×10^{4}		4.3
		CH_3CN		1.4	

---

[a] Oxidation potentials in acetonitrile taken from reference 1.

[b] Pearson nucleophilic reactivity constants taken from reference 6.

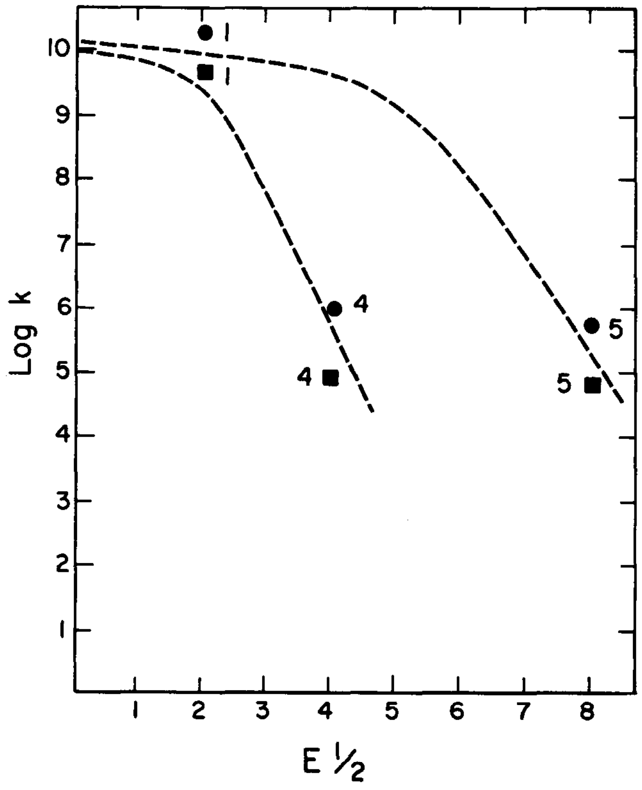


Figure 1: Correlation of rate constants with oxidation potentials, in acetonitrile (●) and in methanol (■).

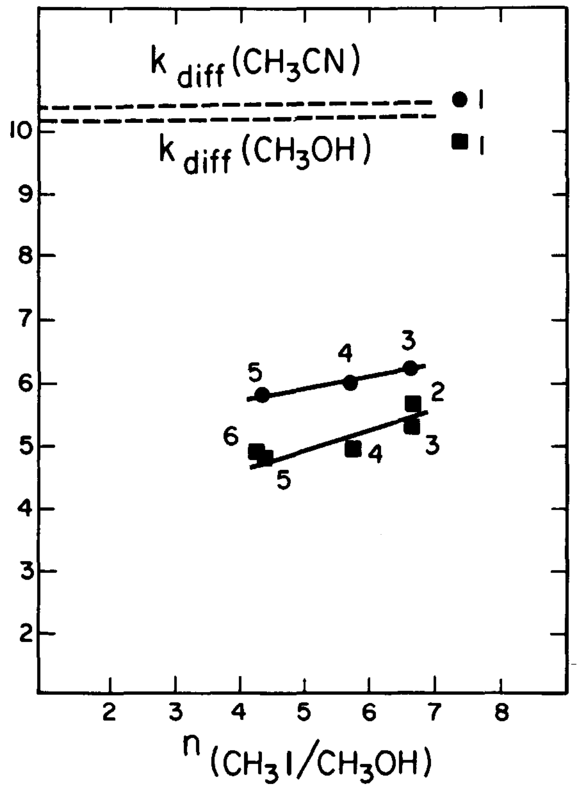
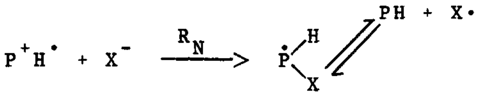


Figure 2: Correlation of rate constants with Pearson nucleophilicity constants, in acetonitrile (●) and in methanol (■).

A good correlation is obtained for bromide, chloride, and the other nucleophiles, excepting iodide, when a nucleophilic reactivity scale[8,9] is used, Figure 2. Therefore, iodide is the only electron donor which clearly reduces perylene radical cation by electron transfer. Chloride and perhaps bromide reduce by a mechanism involving nucleophilic addition. This mechanism is not entirely unexpected since it is well known[10] that free radical additions to aromatics are reversible whenever the radical is more stable than phenyl radical.



The reaction of perylene radical cation with nucleophiles is not very sensitive to changes in nucleophilicity. The slopes in Figure 1 are approximately 0.2, indicating that perylene radical cation is only about one-sixth as sensitive as methyl iodide.

References

1. L. Eberson, *J. Chem. Soc., Chem. Comm.*, 826 (1975).
2. I. N. Roznikov, N. P. Gambaryan, and E. G. Galpern, *Tetrahedron Letters*, 4819 (1976).
3. M. Ottolenghi, *Chem. Phys. Lett.*, *12*, 339 (1971).
4. R. A. Marcus, *Ann. Rev. Phys. Chem.*, 155 (1964).
5. D. Rehm and A. Weller, *Israel J. Chem.*, *8*, 259 (1970).
6. W. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N.Y., 1952.
7. C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York, N.Y., 1970, p. 506.
8. R. G. Pearson, in Advances in Linear Free Energy Relationship, Ed., N. B. Chapman and J. Shorter, Plenum Press, New York, N.Y., 1972, Chapter 6.
9. J. O. Edwards, *J. Amer. Chem. Soc.*, *76*, 1540 (1954).
10. (a) A.L.J. Beckwith, *Organic Chem. Ser. 1*, *10*, 1 (1973); (b) R. A. Jackson, *ibid.*, *10*, 205 (1973), R. A. Jackson, *J. Chem. Soc., Chem. Comm.*, 573 (1974).