Some Comments on the Measurement of the Electronic Nature of Free Radicals by Competition Methods

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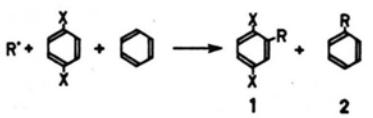
Polar nature of radicals, direct measurement of the latter, interpretation of analytical results

By way of our interest in the reactions of adamantyl [1–3] and cyclohexadienyl radicals [4–6] we have recently directed our attention to techniques of evaluating the electronic nature of such radicals. We wish to comment on the uses and limitations of one commonly applied technique, namely the competition method. This has been used, for example, to study phenylation reactions [7] and more recently the nucleophilic character of bridgehead free radicals [8]. In general the method is based on the simplified reaction scheme below:

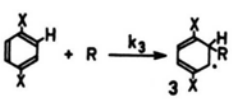


(1)

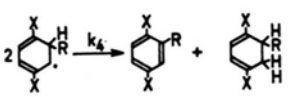
I.e. the chosen radical is allowed to react homogeneously with a standard reference substance and the products **1** and **2** measured, usually by gas chromatography. The ratio **1**/**2** is then taken to be a measure of the polar nature of R· [9].

We wish to point out the danger of interpreting such results solely on this basis. The basic error lies in the assumption that the reaction occurs in a single step [10]. The role of cyclohexadienyl radicals in such reactions is now well documented [10] and hence it is more likely that **1** and **2** arise via reactions (2) and (3).

a: x = substituent,
b: x = H.



(2)



(3)

+ possibly dimeric products.

It is clear therefore that the ratio of end product concentrations will not only be controlled by initial preferences in reactivity but also the difference in the ratio of rate constants for the bimolecular decay of the primary cyclohexadienyl radicals. This effect will clearly place semiquantitative affinity series in doubt since it is highly unlikely that this latter ratio will remain constant along any given series. Thus in the likely event that

$$\frac{k_4 \quad \text{(substituted cyclohexadienyl)}}{k_4 \quad \text{(cyclohexadienyl)}}$$

does *not* remain constant along a series of radicals R then the product yields can do no more than reflect the composite effects of variations in k_3 and k_4 on traversing the series. This is clearly not a measure of the polar nature of R·. One method of overcoming these objections and at the same time enjoying the simplicities of a competition technique would be to measure the relative yields of **3a** and **3b** under conditions in which a. no significant decay of **3a** or **3b** occurs before measurement and b. in which a low stationary state of R· prevents complicating R· und R· reactions. A flash photolytic technique involving photodecomposable compounds *e.g.* peresters as sources of R· would appear applicable.

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[1] W. G. FILBY and K. GÜNTHER, Chem. Phys. Letters **14**, 440, [1972].
[2] W. G. FILBY and K. GÜNTHER, ibid., accepted for publication.
[3] W. G. FILBY and K. GÜNTHER, Z. Naturforsch., in press.
[4] G. O. PHILLIPS, W. G. FILBY, J. S. MOORE, and J. V. DAVIES, Carb. Res. **16**, 105 [1971].
[5] W. G. FILBY and G. O. PHILLIPS, Proc. tenth Ann. Meeting on Radiation Chemistry, Marianske Lazne, vol. III, p. 689 [1970].
[6] K. GÜNTHER, W. G. FILBY, and K. EIBEN, Tetrahedron Letters [London] **3**, 251 [1971].
[7] W. A. PRYOR, „Free Radicals", McGraw Hill Bock Co. New York 1966.
[8] A. MANGINI, P. SPAGNOLO, D. TASSI, M. TIECCO, and P. ZANIRATO, Tetrahedron, [London] **28**, 3485 [1972].
[9] If products **1** and **2** were to arise only by reaction (2) as written then the assumption would hold. However the electron balance alone shows this not to be the case.
[10] S. A. WEINER and G. S. HAMMOND, J. Amer. chem. Soc. **91**, 896 [1969]. For a newer discussion of the factors governing disproportionation and recombination reactions of aromatic radicals see. M. J. GIBIAN and R. C. CORLEY, J. Amer. chem. Soc. **94**, 4178 [1972].