Ion Association in the Base-induced Autoxidation of 9-Substituted Fluorenes in t-Butyl Alcohol

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PREVIOUS investigations[1,2] of the oxidation of fluorene to fluorenone by molecular oxygen in solutions of alkali-metal t-butoxides in t-butyl alcohol indicate that the rate-limiting step of the reaction is the transfer of an electron from the rapidly formed 9-fluorenyl anion to oxygen. We have recently presented evidence suggesting the involvement of ion pairs in this reaction,[2] and we now report results which directly show the importance of ion association in the autoxidation of a series of 9-substituted fluorenes (FlHX; Fl = 9-fluorenylidene, X = CN, CO_2Me, COPh, SO_2Me, SO_2Ph) under the same conditions.

All the compounds examined are completely converted into the related carbanion salt in dilute solutions of alkali-metal t-butoxides ($MOBu^t$) in t-butyl alcohol (10^{-3}—10^{-2}M) as evidenced by the invariance of their visible absorption spectra with changing base concentrations in the absence of oxygen. When oxygen is present, the carbanions are smoothly and quantitatively converted into fluorenone at rates which are conveniently measured spectrophotometrically at 30°.† The rate of disappearance of the carbanion obeys the kinetic equation

$$v = k_{\text{obs}}[\text{FlHX}] = k[\text{O}_2][\text{FlHX}].$$

In most experiments the reaction mixture was saturated with oxygen at a pressure of 760 torr.

Although fully ionised under the reaction conditions, the substrates FlHX (X = CN, COPh, SO_2Me, SO_2Ph) are oxidised at rates which vary with the concentration of the base present. The rate of oxidation of 9-cyanofluorene increases with increasing base concentration, the two sulphones show a more pronounced rate decrease, while the rate of oxidation of 9-benzoylfluorene passes through a minimum value as the base concentration is changed. By using a fixed concentration (0·01M) of sodium t-butoxide, addition of sodium tetraphenylboron (up to 0·01M) brings about similar changes in reaction rate.

The difference in the pattern of kinetic behaviour between 9-cyanofluorene and the sulphones makes it unlikely that these changes are due to changes in the solubility of oxygen in the reaction mixtures. This is supported by our observation that sodium tetraphenylboron (8×10^{-3}M) does not significantly alter the solubility of oxygen in t-butyl alcohol. We therefore ascribe our kinetic observations to participation in the oxidation by both free carbanions and carbanion–alkali-metal ion pairs, the relative proportions of which will depend on the concentration of free alkali-metal cations in the solution. This situation is represented in the Chart, from which it can be deduced that

$$k_{\text{obs}} = (k_{\pm}[\text{M}^+] + k_{-}K_{\text{d}})/([\text{M}^+] + K_{\text{d}}) \qquad (1)$$

where the velocity constants $k_{\pm}$ and k_{-} incorporate the (constant) oxygen concentration.

We have tested this equation using the carbanion sodium salts with X = CN and SO_2Ph. Values of the ion-pair dissociation constant K_{d} were determined by the Fuoss procedure[3] from conductance measurements in t-butyl alcohol to be $4{\cdot}0 \times 10^{-5}$M (X = CN) and $2{\cdot}2 \times 10^{-6}$M (X = SO_2Ph). The concentration of free sodium ion was varied by addition of sodium tetraphenylborate or sodium perchlorate for which ion-pair dissociation constants of $1{\cdot}0 \times 10^{-3}$M and $1{\cdot}0 \times 10^{-5}$M respectively were obtained. By comparison the carbanion salt and the excess of sodium t-butoxide contribute negligibly to the concentration of free sodium ion.[4]

Graphs of $k_{\text{obs}}([\text{Na}^+] + K_{\text{d}})$ against $[\text{Na}^+]$ are shown in the Figure. Their linearity supports our analysis of the reaction mechanism. The observation that points for sodium perchlorate and sodium tetraphenylborate fall on the same line despite the 100-fold difference in K_{d} confirms the view that the changes in oxidation rate are the result of changes in the concentration of the free cation rather than of the salt itself.

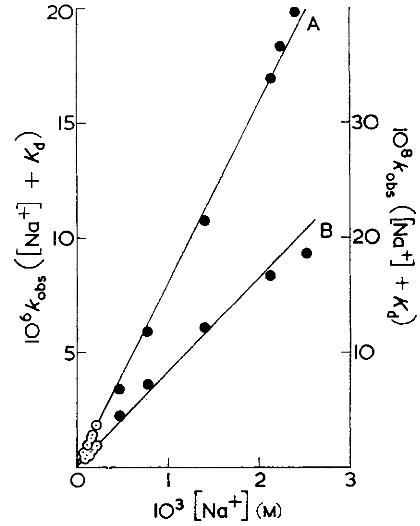

FIGURE. *Test of equation* (1) *using* 9-*cyanofluorene* (*line* A, *left-hand ordinate*) *and* 9-*fluorenyl phenyl sulphone* (*line B, right-hand ordinate*) *in the presence of sodium tetraphenylborate* (●) *and sodium perchlorate* (⊙) *in t-butyl alcohol solutions of sodium t-butoxide saturated with oxygen at* 30°. *Linear regression analysis gives*: *for* 9-*cyanofluorene*, $k_{\pm}$ $8{\cdot}3 \times 10^{-3}$ *sec.*$^{-1}$, k_{-} $6{\cdot}0 \times 10^{-3}$ *sec.*$^{-1}$; *for* 9-*fluorenyl phenyl sulphone*, $k_{\pm}$ $7{\cdot}2 \times 10^{-5}$ *sec.*$^{-1}$, k_{-} $1{\cdot}3 \times 10^{-3}$ *sec.*$^{-1}$.

From the ratio of the intercept to the slope of the lines in the Figure, the relative reactivity of

$$\begin{tikzcd}
\text{FlX}^-\text{M}^+ \arrow[rr, shift left, "K_{\text{d}}"] \arrow[dr, "k_{\pm}", "\text{O}_2"'] & & \text{FlX}^- + \text{M}^+ \arrow[ll, shift left] \arrow[dl, "k_{-}"', "\text{O}_2"] \\
& \text{Fl=O} &
\end{tikzcd}$$

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† The rate of disappearance of the carbanion is equal to the rate of appearance of fluorenone in all cases except when X = CO_2Me, where a metastable intermediate appears to be formed, and when X = SO_2Me, where fluorenone formation is not quantitative.

the free carbanion and ion-pair towards oxygen can be evaluated. For X = SO_2Ph, the free ion is more reactive than the ion pair by a factor of about 20: for X = CN, the ion-pair appears to be slightly the more reactive. Smid has already studied a proton-transfer reaction in which a fluorenyl contact ion-pair shows greater reactivity than the free carbanion.[5] The explanation of such phenomena is as yet a matter for speculation.

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[1] G. A. Russell, A. G. Bemis, E. J. Geels, and E. G. Janzen, Symposium on Oxidation, San Francisco, August, 1967, Preprints p. I-233; G. A. Russell, "Free Radicals in Solution," Butterworths, London, 1967, p. 185.

[2] D. Bethell and R. J. E. Talbot, *J. Chem. Soc.* (*B*), 1968, 638.

[3] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, 1965.

[4] D. Bethell, A. F. Cockerill, and D. B. Frankham, *J. Chem. Soc.* (*B*), 1967, 1287.

[5] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1967, **89**, 2764; J. Smid, *A.C.S. Polymer Preprints*, 1968, **9**, 1063.