Peroxide Catalysed Vinyl Polymerization

IN recent months the importance of the reactivity of the free radicals in polymerization systems has been stressed, in particular the ability of a free radical both to initiate and terminate reaction chains¹. The emphasis, however, has been on the ability of the radical in question to terminate the growing chains², and it is the object of the present communication to direct attention to the lowered rate of initiation of growing chains which results from the use of certain catalysts.

A feature of peroxide catalysed vinyl polymerizations is that the rate of reaction is proportional to the square root of the catalyst concentration. This, however, is true only for catalysts which generate active free radicals, when the catalyst is used over a wide range of concentrations. The results given in the accompanying graph show that in the polymerization of styrene using di-*m*-nitrobenzoyl peroxide, *m*-nitrobenzoyl benzoyl peroxide and di(2,3,4,5-tetrachlorobenzoyl) peroxide this relationship does not hold. Initial rates of reaction were determined, as the rate fell off fairly rapidly with time in the case of these poor catalysts. Benzoyl peroxide gives a good linear agreement. The observed deviation from linearity occurs with catalysts which give radicals of low activity. (It will be shown again that the activity of a radical is related to the distribution of electron density; thus electron repelling substituents increase the reactivity of a radical, and electron attracting substituents lower the reactivity. Mesomeric effects either supplement or reverse the inductive effect, depending on the direction of electron transfer.)

When incorporated in the kinetic scheme:

application of the stationary state method of analysis used by Melville and others³ gives, when the three termination coefficients are considered to be equal (k_t) (the terms having their customary significance):

$$\begin{aligned}
 \Sigma(P_r) &= \frac{k_p'(M)(R.)}{\sqrt{k_i k_t(c)}}, \\
 (R.) &= \frac{k_i(c)}{\{k_p'(M) + \sqrt{k_i k_t(c)}\}}.
 \end{aligned}$$

Thus the reaction-rate:

$$\begin{aligned}
 -\frac{dM}{dt} &= k_p'(M)(R.) + k_p(M)\Sigma(P_r) \\
 &= k_p'(M) \sqrt{\frac{k_i(c)}{k_t}} \left\{ \frac{k_p(M) + \sqrt{k_i k_t(c)}}{k_p'(M) + \sqrt{k_i k_t(c)}} \right\}
 \end{aligned}$$

This reduces to the usual form for zero-order initiation when $k_p' = k_p$. This expression gives a linear relationship between the reaction-rate and the square root of the catalyst concentration only when the concentrations used are very small or when k_p' and k_p are nearly equal. To suggest, as has been done, that the three termination constants are equal is a great over-simplification since, for definite values of k_p and k_t , at low concentrations of catalyst the rate would be dependent upon $\sqrt{k_i(c)}$, which is probably not true. However, preliminary results from the intrinsic viscosities of the polymers indicate that these fall normally with increase in catalyst concentration, as would be predicted from the above scheme.

Also:

$$\begin{aligned}
 \bar{P}_n &= \frac{V(\text{prop.})}{V(\text{init.})} = \frac{(M)\{k_p'(R.) + k_p\Sigma(P_r)\}}{k_p'(M)(R)} \\
 &= \frac{k_p(M)}{\sqrt{k_i k_t(c)}}.
 \end{aligned}$$

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¹ Mayo, F. R., and Gregg, R. A., *J. Amer. Chem. Soc.*, **70**, 1284 (1948).

² Breitenbach, J. W., and Schneider, H., *Ber.*, **76**, B, 1088 (1943); *Chem. Abs.*, (33), 4914 (1944); also *ibid.*, 2416, 4933.

³ For example, Gee, G., and Melville, H. W., *Trans. Farad. Soc.*, **40**, 240 (1944).

Red Lead as a Selective Oxidant

SINCE the fundamental investigations of Dimroth¹, Criegee², Malaprade³ and Fleury⁴, lead tetra-acetate and periodic acid as selective oxidants have played an important part in organic chemistry, particularly for the elucidation of the structure of carbohydrates and related compounds and also from the preparative point of view⁵. It has been found now that red lead (Pb_3O_4) in many cases can be used successfully instead of the above-mentioned oxidants either in aqueous acetic acid medium or in organic solvents containing anhydrous acetic acid. It may be supposed that, in the presence of acetic acid, red lead gives rise with a limited velocity to intermediate formation of lead tetra-acetate which, in the presence of a suitable hydrogen donor, will be promptly reduced to lead diacetate. Therefore, the reaction mixture never contains an excess of tetra-acetate. Hence