

DISPROPORTIONATION-COMBINATION COMPETITION FOR ISOPROPYL-t-BUTOXY RADICAL PAIRS

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We wish to report evidence supporting interpretation of the intercepts of reciprocal yield-fluidity correlations in terms of kinetic parameters.<sup>1</sup> The basis of this interpretation is a phenomenological treatment of the combination-separation competition for the radical pair which is summarized in Scheme I. The present comparison is for *i*-propyl-t-butoxy pairs (R = *i*-pr) generated from the perester<sup>2,3</sup> (1) at 102° and the hyponitrite<sup>4</sup> (2) at 32°. The relationship of interest is equation 1 where  $y_{\text{ether}}$  is the isolated yield of *i*-propyl *t*-butyl ether,  $k_d$  is the formal rate constant for diffusive separation of the radical pair,  $k_c$  is the formal rate constant for combination and  $k_z$  is the rate constant for disproportionation of the pair. The scheme assumes the fluidity ( $1/\eta$ ) dependence is dominated by that for  $k_d$  and is approximately linear with  $(1/\eta)^{1/2}$  in the high viscosity region. At zero fluidity  $k_d$  is also zero so that the yield of combination product should be unity unless another chemical reaction, such as disproportionation, is competitive with combination. The model suggests that the  $k_z/k_c$  ratio should be equal to the intercept of the  $(\frac{1}{y} - 1)$  vs.  $f^{1/2}$  correlation.

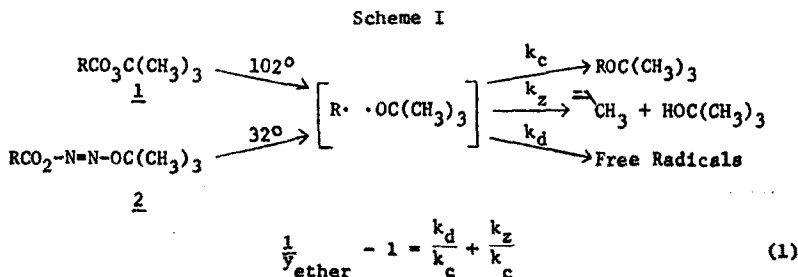


Figure 1 shows such a plot for the ether yields from the two sources (at rather widely different temperatures). The intercepts are both near 2.4 which is the value obtained by Kochi and Sheldon<sup>5</sup> for the photolysis of the perester in decalin. Previous data<sup>1</sup> for methyl *t*-butyl ether yields from the corresponding hyponitrites gave a zero intercept as expected

since no disproportionation is possible in that case.<sup>6</sup> The good agreement of the  $k_2/k_c$  ratio obtained here with the completely independent estimate<sup>5</sup> is important in lending support to the interpretation of similar nonzero intercepts<sup>1,7</sup> for t-butyl peracetate formation from 2 ( $R = CH_3$ ) in terms of the decarboxylation-combination competition. No good alternative means of estimating the ratios are available for that competition.

The slope of the linear part of the present correlations ( $\sim 3 (cP^{-1/2})$ ) is slightly smaller than that estimated for the methyl-t-butoxy pair ( $\sim 5 (cP^{-1/2})$ ) and is consistent with a lower diffusion rate for the larger *i*-propyl radical. The  $\sim 2.4$  intercept of Figure 1 indicates the total fraction geminate reaction (combination plus disproportionation) is larger for secondary alkyls, compared to methyl, because of the additional disproportionation path made available by the alpha hydrogen atoms.

We conclude from these studies that the intercepts of these correlations give reasonable estimates of the importance of a chemical reaction which is competitive with combination rather than of some initial separation distance.<sup>8</sup> The results suggest that the rate constant for combination of *i*-propyl-t-butoxy pairs is not much different from that for methyl-t-butoxy pairs. The effect of radical size on the separation process also appears to be small in the present analysis. The difference between the intercepts and slopes of the correlations for 3 generated by the two sources may be a result of a temperature effect ( $\Delta H_c < 0$ ) or of intervening molecule effect (1,  $CO_2$  vs. 2,  $CO_2 + N_2$ ).

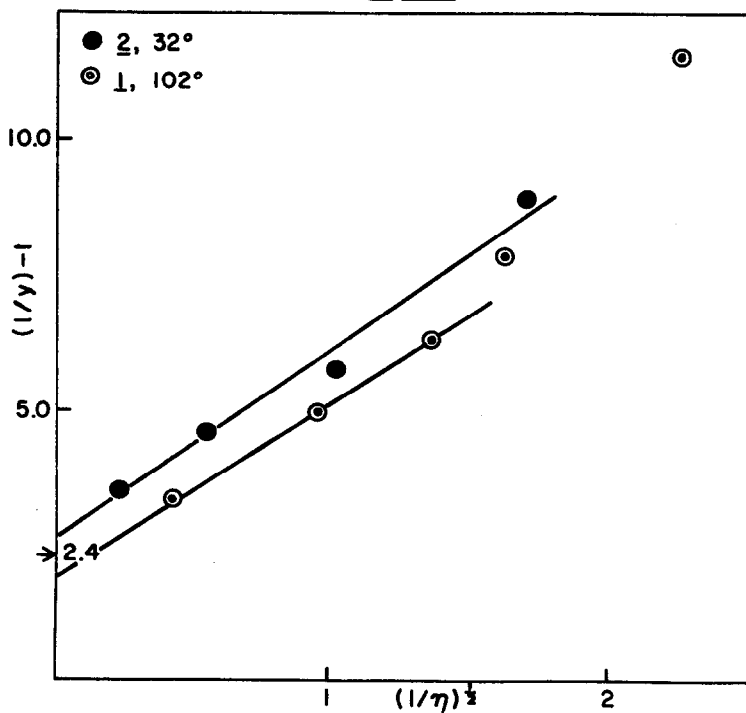
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Table I  
Isopropyl *t*-Butyl Ether Yields<sup>c</sup> From 1<sup>a</sup> and 2<sup>b</sup>

Source	Solvent	$\eta$ (cP)	% Yield
<u>1</u>	Nujol	5.30	.23
<u>1</u>	Nujol:Decane (1:1)	1.07	.17
<u>1</u>	Dodecane	0.52	.14
<u>1</u>	Decane	0.37	.11
<u>1</u>	Heptane	0.08	.08
<u>2</u>	Nujol:CCl <sub>4</sub> :Heptane (5:1:0)	16.99	.22
<u>2</u>	" (7:2:3)	3.55	.18
<u>2</u>	" (2:1:3)	1.01	.15
<u>2</u>	" (0:1:5)	.36	.10

a) 101.8°C, solvents ca. 0.1M styrene. b) 32°C. c) By glpc analysis.

Figure 1



References

- 1) T. Koenig and M. Deinzer, J. Amer. Chem. Soc., 90, 7014 (1968); T. Koenig, ibid., 91, 2558 (1969).
- 2) N. A. Milas and A. Golubovic, ibid., 80, 5994 (1958), P. D. Bartlett and L. B. Gortler, ibid., 85, 1864 (1963).
- 3) The  $\beta$ -secondary deuterium isotope effect for the thermolysis of this perester is 1.20 at 103.4° ( $\beta$ -d<sub>6</sub>) indicating significant i-propyl radical character in the transition state. Oxygen-18 radomization is less than 0.5% so that very little recombination of any isobutyroxy radical intermediates is occurring. The thermolysis of 1 essentially leads directly to 3.
- 4) T. Koenig and W. R. Mabey, J. Amer. Chem. Soc., 92, 3804 (1970).
- 5) R. Sheldon and J. Kochi, ibid., 92, 5175 (1970).
- 6) Upward curvature in the high fluidity region is a common observation<sup>8</sup> even when first power fluidity is used. The power of the fluidity used is not very important in the present example since the first power gives an intercept of 3 which is still acceptable. For the methyl-t-butoxy pair a non zero intercept and downward curvature is obtained using 1/n.
- 7) T. Koenig, J. G. Huntington and R. Cruthoff, J. Amer. Chem. Soc., 92, 5413 (1970).
- 8) O. Dobis, J. M. Pearson and M. Szwarc, J. Amer. Chem. Soc., 90, 278 (1968); F. E. Herkes, J. Friedman and P. D. Bartlett, Int. J. Chem. Kinet., 1, 193 (1969).