

## NOTIZEN

**Distinguishing Kinetically between Reaction Types  $A + B \rightarrow C$  and  $A + 2B \rightarrow C + B$ . The Relevance to the Alcoholysis of Ketenes and Related Reactions**

Derek P. N. Satchell\* and

Marcel J. F. Satchell

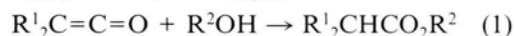
King's College London, Strand, London, WC2R 2LS, U.K.

Z. Naturforsch. **46b**, 391–392 (1991); received November 6, 1990

Kinetics, Mechanistic Distinction, Ketenes

An apparent discrepancy between the kinetics reported for the alcoholysis of ketenes is resolved by examining conditions under which third-order kinetic behaviour can be mistaken for second-order behaviour.

One of us has made a kinetic study of the alcoholysis of ketenes (eq. (1)) using a hydrocarbon solvent [1]. Employing the isolation method (following the loss of ketene with the alcohol present in a substantial excess of the ketene) it was shown that at 25 °C the reaction is kinetically first-order in ketene, and approximately second-order in the stoichiometric alcohol concentration [2],  $[R^2OH]_{\text{stoich}}$ , when  $[R^2OH]_{\text{stoich}}$  lies



between *ca.*  $10^{-2}$  and  $0.2 \text{ mol dm}^{-3}$ . Thus, using the standard first-order rate equation for loss of ketene, doubling  $[R^2OH]_{\text{stoich}}$  in this concentration range leads to a nearly 4-fold increase in the observed first-order rate constant. Such an increase is readily distinguishable from the 2-fold increase that would result were the reaction experimentally first-order in  $[R^2OH]_{\text{stoich}}$ .

Brady, Vaughn and Hoff, in a very similar kinetic study [3], chose not to use the isolation method but to employ comparable initial concentrations (*ca.*  $0.05 \text{ mol dm}^{-3}$ ) of ketene and alcohol, with the alcohol slightly in excess. They reported that their concentration-time data obey the stand-

ard second-order rate equation [4] (eq. (2)) for a reaction of kinetic type  $A + B \rightarrow C$ . In eq. (2) *a* and *b* are the initial concentrations of A and B, respectively, and the other symbols have their usual meaning. Brady *et al.* show rectilinear plots of *t* against  $\ln(a-x)/(b-x)$ . Our study suggests, however,

$$k_2t = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad (2)$$

that the results obtained under such conditions should more nearly obey the (third-order) rate equation for an  $A + 2B \rightarrow C + B$  reaction (eq. (3)). The two studies are therefore in apparent conflict.

$$k_3t = \frac{1}{(a-b)} \left\{ \frac{x}{b(b-x)} + \frac{1}{(a-b)} \ln \frac{a(b-x)}{b(a-x)} \right\} \quad (3)$$

A distinction between  $A + B \rightarrow C$  and  $A + 2B \rightarrow C + B$  processes is frequently important in solution chemistry because a second molecule of one reactant can often participate as a catalyst, especially if it is a potential acid or base [5, 6]. We have now examined conditions under which concentration-time data that accurately satisfy eq. (3) also lead to satisfactory straight line plots when entered instead into eq. (2). The figure shows three specimen plots of eq. (2) using values of *x* and *t* that satisfy eq. (3) for certain chosen values of *a*, *b*, and  $k_3$ . For curve 1  $a = 0.05 \text{ mol dm}^{-3}$ ,  $b = 0.051 \text{ mol dm}^{-3}$ , and  $k_3 = 8 \text{ mol}^{-2} \text{ dm}^6 \text{ t}^{-1}$ . Departures from rectilinearity are evident visually, using reasonable time scales, before the first half-life is reached ( $x = a/2$  when  $t = 70.5$ ). However, a good straight line (correlation coefficient  $r \geq 0.9990$ ) is present until  $x \approx a/4$ . The best straight line through all points shown up to the half-life has  $r = 0.9959$ . The shape of curve 1 (its goodness of fit to a straight line) is unaffected by multiplying either the rate constant  $k_3$ , or both the initial concentrations *a* and *b*, by any chosen factor. This is also true for the other specimen plots shown.

For curve 2  $a = 0.05 \text{ mol dm}^{-3}$ ,  $b = 0.10 \text{ mol dm}^{-3}$ , and  $k_3 = 8 \text{ mol}^{-2} \text{ dm}^6 \text{ t}^{-1}$ . This curve is straighter; it is satisfactorily rectilinear ( $r \geq 0.9990$ ) for more than one half-life ( $x = a/2$  when  $t = 11.9$ ). By two half-lives ( $x = 3a/4$  when  $t = 30.8$ ) *r* has fallen to 0.9980, and departures from rectilinearity are evident visually. However, for larger excesses of B over A the extent of rectilinearity increases, so that distinctions between eq. (2) and (3) become increasingly difficult.

\* Reprint requests to Dr. D. P. N. Satchell.



The curve for the condition  $a = b$  is, as would be expected, very similar in shape to curve 1. Curve 3 corresponds to  $a = 0.1 \text{ mol dm}^{-3}$ ,  $b = 0.05 \text{ mol dm}^{-3}$ , and  $k_3 = 8 \text{ mol}^{-2} \text{ dm}^6 \text{ t}^{-1}$ , so that here reactant A has been placed in a two-fold excess of B (rather than the reverse as in curve 2). Curve 3 exhibits

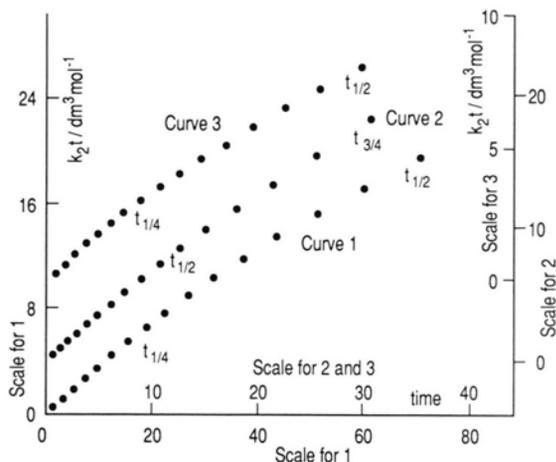


Figure. Plots of eq. (2) using data that satisfy exactly eq. (3). For all curves  $k_3 = 8 \text{ dm}^6 \text{ mol}^{-2} \text{ t}^{-1}$ ; curve 1:  $a = 0.050$ ,  $b = 0.051 \text{ mol dm}^{-3}$ ; curve 2:  $a = 0.050$ ,  $b = 0.10 \text{ mol dm}^{-3}$ ; curve 3:  $a = 0.10$ ,  $b = 0.050 \text{ mol dm}^{-3}$ .

rectilinearity comparable so that of curve 1; at  $t = 8.9$  when  $x = b/4$ ,  $r = 0.9992$ , but by  $t = 29.7$  when  $x = b/2$ ,  $r$  has fallen to  $0.9956$ . Also when A is in excess of B, increasing that excess does not materially increase the extent of rectilinearity, as it does when the initial concentrations are reversed.

To distinguish most easily between eq. (2) and (3) it is desirable therefore to have A in excess of B or, if B must for practical reasons be kept in excess of A, to keep their initial concentrations as similar as possible. For such concentration conditions it is desirable to follow the reaction for at least one half-life, and preferably much further. If we consider the results of Brady *et al.* in this light we find that, although from the information they give [3] it is impossible to be certain, their initial concentrations appear to fall in the region covered by curves 1 and 2, and their extents of reaction to fall either entirely, or very largely, within the corresponding regions where the data provide what would be regarded as visually good straight lines using either eq. (2) or eq. (3). We conclude therefore that Brady's results are probably compatible with our own finding [1] that the alcoholysis of ketenes in hydrocarbon solvents is almost second-order in the stoichiometric alcohol concentration in the concentration range considered.

- [1] G. Donohue, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc. Perkin Trans. 2* **1990**, 1671.
- [2] See also J. Jähme and C. Rüdhardt, *Tetrahedron Lett.* **23**, 4011 (1982).
- [3] W. T. Brady, W. L. Vaughn, and G. F. Hoff, *J. Org. Chem.* **34**, 843 (1969).

- [4] See M. J. Pilling, *Reaction Kinetics*, Clarendon Press, Oxford (1975).
- [5] E. g. D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.* **4**, 231 (1975).
- [6] D. P. N. Satchell and R. S. Satchell, *Z. Naturforsch.* **44b**, 1329 (1989).