

The relative-rate technique for determining rate constants

Martin King (Royal Holloway, University of London, m.king@rhul.ac.uk)

Many chemical reactions in environmental media are kinetically controlled, that is, their concentration in the environment is limited by their rate of reaction. This is especially true in the field of atmospheric chemistry. Measurement of the rate constant for a reaction is thus important. One method made popular by Atkinson (1) in the atmospheric sciences is the relative-rate technique, which is particularly useful in cases where the concentrations of one reactant are difficult to measure.

The relative-rate technique measures the loss of a substrate compound (S) relative to that of a reference compound (R), both mixed in the same reaction vessel in the presence of a reactive species. With knowledge of the rate constant, k , for reaction between the reactive species and R, one can infer the rate constant of the reactive species with S. The advantage is that reactive species, which often have short lifetimes and are present in very low concentrations, need not be measured. The vessel may be an atmospheric air parcel, an ice core or a reaction chamber. In the following, I consider the reactions of an important night-time atmospheric oxidant, the nitrate radical NO_3 :



Derivation

The rate equations can be written as

$$\frac{d\ln[S]}{dt} = -k_A[\text{NO}_3] \quad (1)$$

$$\frac{d\ln[R]}{dt} = -k_B[\text{NO}_3] \quad (2)$$

Equations (1) and (2) are integrated to

$$\ln[S]_t = -k_A \int_{t=0}^t [\text{NO}_3] dt + \ln[S]_{t=0} \quad (3)$$

$$\ln[R]_t = -k_B \int_{t=0}^t [\text{NO}_3] dt + \ln[R]_{t=0} \quad (4)$$

and rearranged to

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) = -k_A \int_{t=0}^t [\text{NO}_3] dt \quad (5)$$

$$\ln\left(\frac{[R]_{t=0}}{[R]_t}\right) = -k_B \int_{t=0}^t [\text{NO}_3] dt \quad (6)$$

Equations (5) and (6) can be equated to give

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) = \frac{k_A}{k_B} \ln\left(\frac{[R]_{t=0}}{[R]_t}\right) \quad (7)$$

Thus, a plot of $\ln([S]_{t=0}/[S]_t)$ versus $\ln([R]_{t=0}/[R]_t)$ should be a straight line with a gradient of k_A/k_B and an intercept of zero. Knowledge of k_B allows k_A to be determined. An example of such a plot is shown in **Figure 1**, where the reaction rate constant for reaction of the NO_3 radical with some unsaturated carbonyls is calculated relative to the reaction with ethane (2).

Adaptation to the tracer

When sampling a reaction chamber for the concentrations of S and R, imperfect mixing in the changer or loss of R and S owing to the measurement technique may affect the determination of k_A/k_B . Imperfect mixing or loss of material on analysis can be compensated by an internal standard chemical compound I. The concentration of this internal standard [I] is used to account for any dilution of concentration of S and R by sampling.

The term $D_t = \ln\left(\frac{[I]_{t=0}}{[I]_t}\right)$ can be used to adapt equation (7) to

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) - D_t = \frac{k_A}{k_B} \left(\ln\left(\frac{[R]_{t=0}}{[R]_t}\right) - D_t \right) \quad (8)$$

Thus, a plot of $\ln([S]_{t=0}/[S]_t) - D_t$ versus $\ln([R]_{t=0}/[R]_t) - D_t$ will be a straight line with a gradient of k_A/k_B and an intercept of zero. An example is shown in (3).

Regression and analysis of errors

The regression used in Figure 1 to calculate the gradient and intercept must consider the errors in the ordinate and the abscissa. More information can be found in (4). The error in the quantity $\ln([S]_{t=0}/[S]_t) - \ln([I]_{t=0}/[I]_t)$ can be calculated by propagation of errors (5) as

$$\delta_Y = \sqrt{\left(\frac{\delta_S}{[S]_{t=0}}\right)^2 \left(1 + \left(\frac{[S]_{t=0}}{[S]_t}\right)^2\right) + \left(\frac{\delta_I}{[I]_{t=0}}\right)^2 \left(1 + \left(\frac{[I]_{t=0}}{[I]_t}\right)^2\right)} \quad (9)$$

First-order loss of substrate

In some reaction systems the substrate S may not be stable, may irreversibly react with a wall, or may decay away, i.e. it has a first-order loss



Following the same analysis as in the derivation section yields

$$\frac{1}{(t-t_0)} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) = \frac{k_A}{k_B(t-t_0)} \left(\ln \left(\frac{[R]_{t=0}}{[R]_t} \right) - D_t \right) + k_c \quad (10)$$

The equation now requires the time, t since the reaction began at time t_0 to be recorded. Plotting the left-hand side term in equation (10) against the first term on the right yields a straight line with an intercept of k_c . Plotting data in the form of equation (10) is a method of testing if S is stable in the reaction system.

Concentration of reactive intermediate

There is an issue with the above method of analysis of k_A when there is an extra first-order loss which can be seen during the derivation of (10),

$$\frac{1}{k_A} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) - k_c(t-t_0) = \int_{t=0}^t [NO_3] dt \quad (11)$$

If the nitrate radical concentration, $[NO_3]$, does not change during the experiment, then points on a plot

$$\frac{1}{(t-t_0)} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) \text{ versus } \frac{1}{(t-t_0)} \left(\ln \left(\frac{[R]_{t=0}}{[R]_t} \right) - D_t \right)$$

will cluster together and make the determination of k_A/k_B difficult. More information can be found in (6).

Conclusion

The relative-rate method is a powerful method for determining rate constants needed for lifetime calculations and environmental persistence, especially when one of the reactants—in the above example, $[NO_3]$ —is very difficult to measure. The method is less precise than an absolute kinetic determination, because the

uncertainty of the reference reaction influences the uncertainty of the measured reaction.

References

1. R. Atkinson, *Chem. Rev.*, 1986, 86, 69.
2. C. E. Canosa-Mas, S. Carr, M. D. King, D. E. Shallcross, K. C. Thompson, R. P. Wayne, *Phys. Chem. Chem. Phys.* **1**, 4195 (1999).
3. C. E. Canosa-Mas, M. D. King, P. J. Scarr, K. C. Thompson, R. P. Wayne *Phys. Chem. Chem. Phys.* **1**, 2929 (1999).
4. T. Brauers, B. J. Finlayson-Pitts, *Int. J. Chem. Kinet.* **29**, 665 (1997).
5. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
6. C. E. Canosa-Mas, M. D. King, D. E. Shallcross, R. P. Wayne, *Phys. Chem. Chem. Phys.* **1**, 2411 (1999).
7. M. King, DPhil Thesis, University of Oxford (1998).

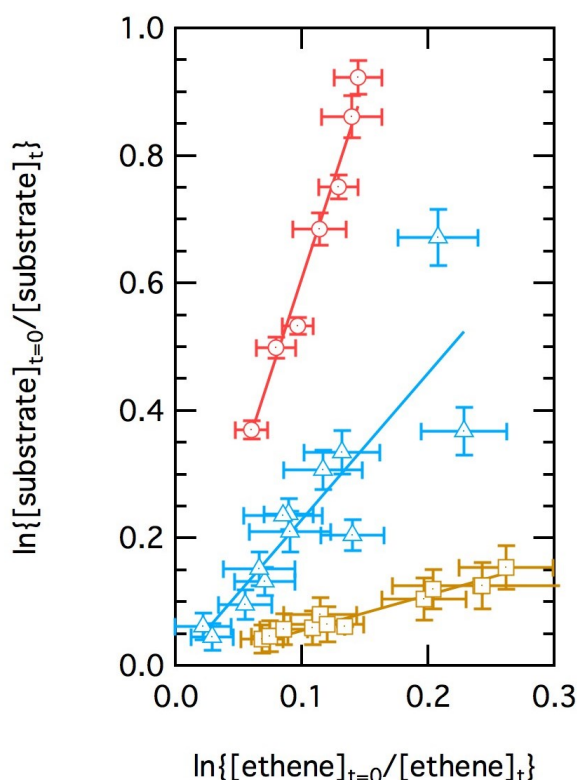


Figure 1. The relative-rate plot for the reaction of some alpha-beta carbonyls with nitrate radical, with ethane as a reference compound. Red circles, acrolein; blue triangles, methyl vinyl ketone; yellow squares, methyl acrylate. From (7).