Parameterization of Complex Reaction Systems: Model Fitting vs. Fundamental Kinetics

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Computer simulation has found increasing application in both the chemical plant and the laboratory for the description of complex reaction and transport systems (Himmelblau et al., 1967, 1968). In the former case it is generally recognized that the rate equations and parameters used to describe the kinetics of the reactions represent a gross oversimplification of the chemistry and merely provide a convenient way of reproducing numerically the observed behavior of the process. For laboratory studies of processes of industrial interest where the transport can be better understood and held under closer control, attempts have been made to fit the data to more detailed chemical models. A number of parameter fits to such extended models have been published. In many of these there is a mistaken belief that the ability to achieve such a fit is, of itself, an indication of the correctness of the model and that the parameters obtained are of fundamental significance.

The result is an ever increasing danger of the proliferation of misleading rate constants in the literature, a situation to which we would like to call attention in this paper.

Among many in the literature, an excellent illustration of parameterization techniques applied to laboratory systems is a recent paper of Herriott, Eckert, and Albright (1972), who studied the kinetics of propane pyrolysis in a tubular plug-flow reactor. They constructed a kinetic model of this process involving 15 fundamental free radical reactions to which parameters which best described the experimental results were assigned. The kinetic equations were solved numerically by a technique originated by Snow (1966). The rate parameters derived from this study which are reported as rate constants give a reasonable fit to the data and provide a useful empirical model for the experiments studied. However, many of them are substantially at variance with the best experimental and theoretical values available in the literature for the fundamental reactions used. Discrepancies such as these are due mainly to the inability of simplified models to describe adequately the complexity of the systems under investigation; errors in some of the numerical techniques used to solve the kinetic equations may also contribute to the deviations.

Let us first examine the possible contribution for which numerical methods may be held responsible. Snow's procedure, which is typical of those employed, uses a standard numerical integration of the kinetic equations combined with a quasi steady state approximation when the derivative of one (or more) of the free radical intermediates becomes small. The errors inherent in this computational approach have become increasingly apparent over the years and have recently been reviewed (Edelson, 1973). Workers in computational kinetics have increasingly turned to an integration method originated by Gear (1971) which works extremely well for the stiff differential equations which are commonly encountered, and which is free of the problems which plague the steady state approximation. We have applied this method to the model proposed by Herriott et al., using one of the sets of conditions reported in their paper; the results are shown in Figure 1. It should be noted that the steady state condition never occurs simultaneously for all three hydrocarbon radicals, and the $H^{\cdot}$ atom never goes into a steady state at all! Despite the therefore dubious applicability of the Snow procedure, a comparison of the conversions and products distributions we obtained with those published in their paper showed surprisingly good agreement (Table 1, columns A and B.). The burden of the disagreement in rate parameters must therefore be laid to the model; however, this instance of agreement between complete integration and steady state approximations must not be construed as lending general validity to the latter procedures.

On the other hand, we have taken a fundamental approach to the same problem and have recently developed an extensive set of reactions to account for the pyrolysis of propane (Allara and Edelson, 1972). These reactions comprised processes of initiation, radical decomposition, chain transfer and radical addition to nonradical species, and radical-radical termination. The set was constructed

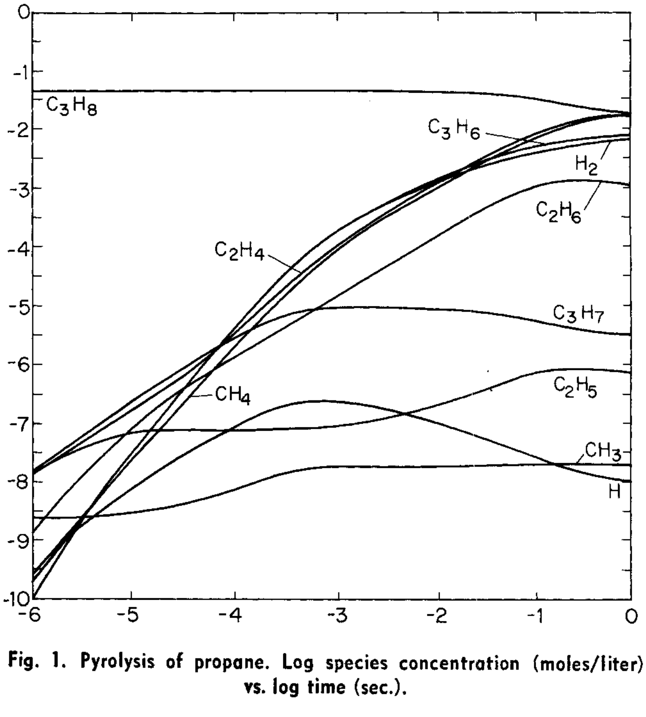

Fig. 1. Pyrolysis of propane. Log species concentration (moles/liter) vs. log time (sec.).

TABLE 1. PROPANE PYROLYSIS, 800°C, 0.5 ATM

	A	B	C	D
Low conversion	19%	19%	19%	15%
Time, s	0.05	0.048	0.029	0.05
Product yields				
Hydrogen	0.188	0.192	0.294	0.205
Methane	0.298	0.297	0.120	0.308
Ethane	0.028	0.024	0.100	0.012
Ethylene	0.266	0.272	0.346	0.267
Propylene	0.219	0.216	0.121	0.205
High conversion	71%	71%	71%	70%
Time	0.55	0.557	0.183	0.55
Product yields				
Hydrogen	0.115	0.118	0.226	0.136
Methane	0.380	0.374	0.210	0.384
Ethane	0.020	0.016	0.060	0.021
Ethylene	0.349	0.359	0.415	0.328
Propylene	0.134	0.133	0.070	0.130

A. Model and calculations of Herriott et al.

B. Model of Herriott et al., integrated by Gear procedure.

C. Model of Allara and Edelson (1972), calculated for conditions of Herriott et al.

D. Experimental data of Herriott et al.

by starting with a primary decomposition of propane into methyl and ethyl radicals. The radicals were then allowed all the kinds of reactions with propane, giving rise to new radical and nonradical species. As new species were developed, they were also allowed to enter into all the types of reaction, and the tree of processes and species continued. This tree can of course be continued indefinitely; it rapidly gives rise to an exponentially increasing number of possibilities. For this study, the tree was arbitrarily terminated at 240 reactions, involving 19 different radicals and 20 nonradical species. Independently evaluated rate constants for many of these reactions are available from the literature (for example, see Garvin, 1971). Otherwise they were estimated from known thermochemical data and/or measured values for analogous reactions by well established techniques (Benson, 1968). This set gave excellent agreement, for example, with the well controlled experiments of Leathard and Purnell (1968), both in product distributions and the complete time history of the pyrolysis without adjusting any of the rate constants. Yet this set applied to the conditions reported by Herriott et al. could not reproduce their experiments (Table 1, columns C and D). We conclude from this that their system must be more complex than even our large set of reactions would indicate. For example, processes which are unimportant in the 500 to 550°C range studied by Leathard and Purnell may have to be included at the higher temperatures used here; furthermore, the participation of the steam carrier in the reaction system remains an unanswered question. In addition, other effects such as wall reactions and local thermal nonequilibrium still have to be investigated, as well as the possibility of deviations from plug flow in the reactor.

Our purpose in pointing out these discrepancies is to emphasize an important aspect of the application of chemical kinetics to engineering problems. The ability to fit a set of numbers to a functional form resembling chemical kinetic equations cannot of itself establish the validity of the model. This point is clearly established in a recent analysis of the mathematical structure of chemical kinetic systems (Feinberg, 1972): even if measurements of all species (including the intermediate radicals—clearly a formidable experimental requirement) throughout the course of the reaction were available, this information by itself is still insufficient to uniquely define the reaction matrix. It cannot be emphasized too strongly that while parameters derived by model fitting serve a useful purpose in providing a numerical description of a set of experimental data, they must not be considered to have the stature of true rate constants. The latter is only achieved after extensive evaluation of data from well understood experiments on several related systems involving different mixes of reactions, and over a wide range of conditions; consistency with theoretical factors must also be considered. Kittrell (1970), in a recent review of modeling procedures, is very careful to reiterate the distinction between fundamental mechanisms and models chosen for simulation purposes and cautions against attempts to read too much of fundamental significance into the results of the latter type of mechanistic approach. On the other hand, Seinfeld and Gavalas (1970, 1972) seem to be proponents of the idea that such derived parameters have some fundamental value even when they are based on data of dubious quality. We believe that it is most important to distinguish between the correlative value of parameter fits as opposed to the predictive capabilities of a truly fundamental model. In particular, one should be most cautious in attempting to apply the results of an ad hoc model beyond the range of the data from which they were derived. We especially object to the publication of these parameters as rate constants, a term which implies a fundamental property of the reaction, since this only further aggravates an already confused situation in the literature.

LITERATURE CITED

Allara, D. L., and D. Edelson, "Computational Modeling of the Thermal Decomposition of Small Alkane Molecules," paper presented at meeting of American Chemical Society, New York (Aug., 1972).

Benson, S. W., *Thermochemical Kinetics,* Wiley, N. Y. (1968).

Edelson, D., "On the Solution of Differential Equations Arising in Chemical Kinetics," *J. Comp. Physics,* **11,** 455 (1973).

Feinberg, M., "On Chemical Kinetics of a Certain Class," *Arch. Rational Mech. Anal.,* **46,** 1 (1972).

Garvin, D., "A Catalog of Compilation and Data Evaluation Activities in Chemical Kinetics, Photochemistry and Radiation Chemistry", CODATA 3 Bulletin, Intern. Council of Scientific Unions (1971).

Gear, C. W., "The Automatic Integration of Ordinary Differential Equations," *Comm. ACM,* **14,** 176 (1971).

Herriott, G. E., R. E. Eckert, and L. F. Albright, "Kinetics of Propane Pyrolysis," *AIChE J.,* **18,** 84 (1972).

Himmelblau, D. M., C. R. Jones, and R. B. Bischoff, "Determination of Rate Constants for Complex Kinetic Models," *Ind. Eng. Chem. Fundamentals,* **6,** 539 (1967).

Himmelblau, D. M., and R. B. Bischoff, *Process Analysis and Simulation,* Wiley, N. Y. (1968).

Kittrell, J. R., in *Advances in Chemical Engineering,* Vol. 8, p. 98, Academic Press, N. Y. (1970).

Leathard, D. A., and J. H. Purnell, "The Self-Inhibited Pyrolysis of Propane at Small Extents of Reaction," *Proc. Roy. Soc.,* **A305,** 517 (1968).

Seinfeld, J. R., and G. R. Gavalas, "Analysis of Kinetic Parameters from Batch and Integral Reaction Experiments," *AIChE J.,* **16,** 644 (1970).

———, Letter to the Editor, *Ind. Eng. Chem. Fundamentals,* **11,** 429 (1972).

Snow, R. H., "A Chemical Kinetics Computer Program for Homogeneous and Free Radical Systems of Reactions," *J. Phys. Chem.,* **70,** 2780 (1966).

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