Thermochimica Acta, 33 (1979) 387—389 387
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Note

REMARKS ON THE EVALUATION OF NON-ISOTHERMAL KINETIC RESULTS

ERHARD KOCH and BERTHOLD STILKERIEG

Institut für Strahlenchemie, Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d Ruhr (B.R.D.)

LARS CARLSEN

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

(Received 19 December 1978)

For nearly two decades, the fundamental kinetic equation

$$\frac{dC}{dt} = A \exp(-E/RT)\, f(C) \tag{1}$$

(C = concentration or fractional conversion) has been used for interpreting and evaluating non-isothermal kinetic curves. While the validity of eqn. (1) was demonstrated by some authors [2—5], it was criticised by others [1] who proposed to treat it as a constitutive equation by using the total differential

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial t}\right)_T + \left(\frac{\partial C}{\partial T}\right)_t \left(\frac{dT}{dt}\right) \tag{2}$$

However, Norwisz [6] has recently revived the controversy by deriving from eqns. (1) and (2) the expression

$$dC/dt = A \exp(-E/RT)\, f(C)\, F(T, T_0, E) \tag{3}$$

$$F(T, T_0, E) = 1 + E(1 - T_0/T)/RT$$

We now find from DTA experiments that the kinetic eqn. (1) — when it involves a linear increase of temperature [7] — satisfactorily describes elementary reactions in solution. We have demonstrated the applicability of eqn. (1) for DTA reaction analysis by evaluating non-isothermal results originating from more than 600 individual experiments, involving 90 reactions of different orders and types in a variety of solvents (C: 10^{-3}—1 M) [7,8].

In order to further study the applicability of eqn. (1) compared to that of eqn. (3), we have extended our computer simulation programs [8—10] — which allow a rapid calculation of theoretical non-isothermal signals of any reaction assumed — by introducing the function $F(T, T_0, E)$ (eqn. 3).

We here report on kinetic data of some uni- and bimolecular reactions (Table 1). The kinetic data have been derived by the following procedure:

TABLE 1

Kinetic data for some uni- and bimolecular reactions studied by DTA compared to reported isothermally obtained values

Reaction [a]	Isothermal values		Computational evaluation (cf. Borchardt and Daniels [11])		Theoretical simulation of experimental curves (eqn. 1)		Theoretical simulation of experimental curves (eqn. 3)	
	E [b]	log A [c]	E	log A	E	log A	E	log A
A	114	15.6	106	14.1	114	15.3	84	10.0
B	110	15.6	120	16.6	116	15.8	77	9.1
C	89	14.0	84	12.5	88	13.2	34	3.5
D	54	5.9	54	5.8	55	5.8	31	1.3
E	118	13.9	108	12.4	108	12.4	67	6.4

[a] A and B, decomposition of benzenediazonium sulfate and 2-methyl-benzenediazonium sulfate, respectively [13]; C, decomposing of *p*-ethoxy-phenyl-pentazole [14]; D, reaction between benzoylchloride and methanol [15]; E, decomposition of 5-phenyl-1,2,3,4-thiatriazole [16].

[b] Activation energies in kJ mole^{-1}.

[c] Arrhenius factors in sec^{-1}; M^{-1} sec^{-1} (reaction D).

(1) computational evaluation of the experimental DTA curves according to Borchardt and Daniels [11];

(2) theoretical simulation (optimum fitting by variation in activation data and reaction enthalpy) [8,10] of the experimental DTA curves, using eqn. (1);

(3) as (2), but using eqn. (3).

The above results clearly demonstrate the excellent agreement generally found between reported isothermally derived results stemming from evaluation due to eqn. (1), in contrast to evaluation based on eqn. (3). Particularly in view of the fact that no experimental verifications have been reported, the assumed applicability of eqn. (3) seems to be utterly unfounded. It should in this connection be noted that this discrepancy was predictable, as even relatively small temperature intervals (40—80 K) would cause a drastic increase of the F-factor.

On the available basis it is obvious that the term $(\partial C/\partial T)_t$ in eqn. (2) is vanishingly small *, if not zero [12]. Consequently, the use of eqn. (2) is restricted to isothermal conditions, but is incorrect for non-isothermal conditions. There is no evidence against the validity of equations derived directly from eqn. (1), such as the Borchardt—Daniels equation [11], which may be readily applied for evaluating DTA curves of quasi-elementary reactions in homogeneous solutions.

---

* The temperature dependence of the volume has to be considered in unfavourable cases, but the deviations in general correspond to a reduction of the activation energy obtained by less than 1 kJ mole^{-1} only.

ACKNOWLEDGEMENTS

We are grateful to the Danish Natural Science Research Council for generous financial support, and to Mr. G. Lindner for technical assistance.

REFERENCES

1 J.R. McCallum and J. Tanner, Nature (London), 225 (1970) 1127.
2 G. Gyulai and E.J. Greenhow, Thermochim. Acta, 5 (1973) 481.
3 E.L. Simmons and W.W. Wendlandt, Thermochim. Acta, 3 (1972) 498.
4 J. Kratochvil and J. Šesták, Thermochim. Acta, 7 (1973) 330.
5 J. Šesták and J. Kratochvil, J. Therm. Anal., 5 (1973) 193.
6 J. Norwisz, Thermochim. Acta, 25 (1978) 123.
7 E. Koch, Non-isothermal Reaction Analysis, Monograph, Academic Press, New York, 1977.
8 E. Koch, B. Stilkerieg and L. Carlsen, to be published.
9 E. Koch and B. Stilkerieg, Thermochim. Acta, 17 (1976) 1.
10 E. Koch and B. Stilkerieg, Thermochim. Acta, 27 (1978) 69.
11 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
12 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
13 M.L. Crossley, P.H. Kienle and C.H. Benbrook, J. Am. Chem. Soc., 62 (1940) 1400.
14 R. Huisgen and I. Ugi, Chem. Ber., 90 (1957) 2914; I. Ugi and R. Huisgen, Chem. Ber., 91 (1958) 531.
15 J.C. Biordi, J. Chem. Eng. Data, 15 (1970) 166.
16 A. Holm, L. Carlsen and E. Larsen, J. Org. Chem., in press.