COMMENTS

Comment on “Kinetics of a Diels–Alder Reaction of Maleic Anhydride and Isoprene in Supercritical CO_2”

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The purpose of this Comment is to correct an analysis of data in the Ph.D. thesis of G. C. Alexander[1] reported by Glebov et al.[2] in the Appendix and Figure 1 of ref 2. Specifically, Glebov et al. recalculated rate constants measured by Alexander and Paulaitis[1,3] for the Diels–Alder reaction of maleic anhydride (MA) with isoprene in supercritical CO_2. In addition to the raw kinetic data in Appendix C of ref 1, they used the results of a gas chromatograph (GC) calibration given in Appendix B. This calibration was done to determine the GC response to MA relative to the reaction product, methylcyclohexene dicarboxylic anhydride (MCDA). Eleven standard solutions of varying MA:MCDA compositions were prepared, and the GC output (area fraction of MA) as a function of MA weight fraction was tabulated in Appendix B. An expression for the weight fraction of MA in terms of MA area fraction was also obtained by a nonlinear least-squares fit of these data. The fitted parameters were also reported in this appendix. Although this is explained in the text of Appendix B, two column headings in the table of results for the grams of MA and the grams of MCDA in the standard solutions were inadvertently transposed, except for the last two entries, which are under the correct column headings. Glebov et al. used this expression with the reported parameters in their analysis, but assumed the calibration was done for the reaction product, MCDA. Their recalculation of rate constants (in mole fraction units) measured by Alexander and Paulaitis yielded $k_x \approx 50\ h^{-1}$ at 60 °C and 100 atm, which is substantially higher than the rate constant they measured at these conditions: $k_x = 17.0 \pm 1.3\ h^{-1}$. However, if the correct GC calibration is used, the rate constants reported originally by Alexander and Paulaitis[1,3] are obtained. These rate constants were measured at 60 °C over a range of pressures from 133 to 410 atm; extrapolating them to 100 atm gives $k_x \approx 10\ h^{-1}$.

Glebov et al. interpret the discrepancy between their measured rate constant, $17.0 \pm 1.3\ h^{-1}$, and the value they obtained from data in ref 1, $50\ h^{-1}$, in terms of the phase behavior or solubility of MA in supercritical CO_2 at 60 °C and high pressures. They argue that the lower value, $17.0 \pm 1.3\ h^{-1}$, was measured in a single, supercritical phase, whereas the higher value, $50\ h^{-1}$, was derived from measurements in a two-phase region. This interpretation is supported by their observation of a sharp increase in the apparent reaction rate constant at 60 °C and 100 atm when a two-phase equilibrium is obtained by increasing the initial MA mole fraction. See Figure 4 in ref 2. As stated above, however, a correct analysis of the GC calibration data in ref 1 gives an extrapolated value of $k_x \approx 10\ h^{-1}$ at 60 °C and 100 atm, which is lower than that obtained by Glebov et al. This result contradicts the observation of a higher apparent reaction rate in the two-phase region at 60 °C and 100 atm if the interpretation by Glebov et al. is correct; i.e., the measurements carried out at 60 °C by Alexander and Paulaitis were under conditions of two-phase equilibrium. The retrograde solubility measurement reported by Glebov et al. is indeed an interesting possibility, and we concur with their suggestion that a detailed study of this behavior may improve our understanding of the pressure dependence of the reaction kinetics for this model Diels–Alder reaction in supercritical CO_2 at 60 °C.

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References and Notes

(1) Alexander, G. C. Ph.D. Thesis, University of Delaware, 1985.
(2) Glebov, E. M.; Krishtopa, L. G.; Stepanov, V.; Krasnoperov, L. N. *J. Phys. Chem. A* **2001**, *105*, 9427.
(3) Alexander, G. C.; Paulaitis, M. E. *Pure Appl. Chem.* **1987**, *59*, 61.

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