Reply to Comment on "Kinetics of a Diels−Alder Reaction of Maleic Anhydride and Isoprene in Supercritical CO_2"

Evgeni M. Glebov, Larisa G. Krishtopa,
Victor Stepanov, and Lev N. Krasnoperov*

*Department of Chemistry and Environmental Science,
New Jersey Institute of Technology, University Heights,
Newark, New Jersey 07102*

Received: February 21, 2003; In Final Form: July 1, 2003

We appreciate the clarification of the origin of the problem that was encountered[1] in the recalculation of the rate constants of the reaction of maleic anhydride with isoprene in carbon dioxide as a process medium from the raw data published in ref 2. According to the explanation offered in the preceding Comment[3] the reason for the difficulties in obtaining the rate constants published in ref 4 from the raw data of ref 2 stems from the (partial) mislabeling of the columns in the thesis of G. C. Alexander (ref 2). We confirm that, when interpreted as suggested in the Comment (i.e., that in Appendix C of ref 2 the column for the weight of maleic anhydride (MA) is labeled as the weight of methylcyclohexene dicarboxylic anhydride (MCDA), the reaction product, and the column for the weight of MCDA is labeled as the weight of MA, with the exception of the two last rows where the numerical information corresponds to the column headings), the rate data from the ref 4 are reproduced.

The major point of our paper (ref 1) is that the measurements in the earlier studies (refs 2 and 4) were performed in a multiphase system. The Comment erroneously implies that this conclusion is based on (or is supported by) the observation that the apparent rate constant observed in our experiments in the multiphase region is larger than the true rate constant in the supercritical phase measured at very low mole fractions of the reactants. Throughout our paper (ref 1) we compare our results with both the rate constants reported in ref 1 and the rate constants obtained from the raw data of ref 2 based on the original headings of the tabulated data. In both cases a significant discrepancy between our measurements and the previous measurements exists. However, our conclusions were not made on the basis of the relative sign of this discrepancy, as could be derived from the Comment. On the contrary, several brief discussions are offered (ref 1) on the difficulties in the assessment of the impact of the second phase on the overall reaction rate, on the adequacy of the sampling procedure, and subsequently, on the measured apparent rate constant.

"The presence of a second (liquid) phase could affect the reaction rate in several ways. Both acceleration and deceleration of the overall reaction are possible, depending on both the reaction rate constants in the two phases and their compositions. If the liquid phase is enriched by both reactants, then the acceleration of the overall reaction is anticipated even for equal intrinsic reaction rate constants in both phases. If the reactants are partitioned between the two phases, then the deceleration of the overall reaction could be expected. And, finally, the rate constants in the supercritical and the liquid phases could differ due to the solvent effects." (Reference 1, p 9428).

"An additional reason for the difference in the apparent rate constants measured in two-phase systems could be in the difference in experimental procedures used. In the current work, the mole fractions of isoprene in the samples obtained from the gas phase were measured (Figure 3b). In refs 6, 7, both maleic anhydride (MA) and MCDA were sampled from the gas phase, but only the ratios of the mole fractions of MA and MCDA in the samples are available.[7] In a two-phase system, the ratio of the mole fractions of two components in the gas phase is not necessarily equal to the ratio of their mole fractions in the overall system.

In addition, in two-phase systems the sampling procedure used in both earlier[6,7] and this work is not well-defined. Stirring the reaction mixture could (and, presumably, does) lead to the formation of small aerosol-like particles of the liquid phase with a long sedimentation time. For example, estimated sedimentation time for micron-sized particles is ca. 2 h. After stirring is stopped, these aerosol-like particles are still sampled together with the gas phase. The samples obtained in this way might reflect the composition intermediate of these of the supercritical and the liquid phases." (Reference 1, p 9433, refs 6 and 7 in this quotation correspond to ref 4 and 2 here).

The major conclusion made in ref 1 is that the measurements in the previous studies were performed under multiphase conditions. This conclusion is based on the dependence of the apparent rate constant on the reactant concentrations (Figure 4 of ref 1), on the direct measurements of the solubility of maleic anhydride in supercritical carbon dioxide (Figure 5 of ref 1), and most importantly, on the *direct observation of the second, liquid phase* at the experimental conditions of the previous studies (experiments 4 and 5, Table 1 of ref 1). Conclusions in ref 1 were derived from these major experimental observations, not from the discrepancy in the absolute values of the apparent rate constants. These experimental observations are mutually consistent and unambiguously demonstrate the existence of two phases under the conditions of the earlier studies (refs 2 and 4).

Our results suggest that the earlier results on the kinetics and the pressure dependence of this reaction should be revised. The effect of pressure on the rate constant is used to derive the "volume of activation" and is one of the major dependences that are used to compare the experiment with the absolute rate theories. Our preliminary data (refs 1 and 5) on the pressure dependence of the rate constant of reaction of maleic anhydride with isoprene in supercritical carbon dioxide, obtained at the experimental conditions that ensure a single supercritical phase, indicate strong *negative* pressure dependence of the rate constant, in contrast with the earlier results (refs 2 and 4) where *positive* pressure dependences were observed.

References and Notes

(1) Glebov, E. M.; Krishtopa, L. G.; Stepanov, V.; Krasnoperov, L. N. *J. Phys. Chem. A* **2001**, *105*, 9427.

(2) Alexander, G. C. Ph.D. Thesis, University of Delaware, 1985.

(3) Paulitis, M. E.; Alexander, G. C. *J. Phys. Chem. A* **2003**, *107*, 9248.

(4) Alexander, G. C.; Paulaitis, M. E. *Pure Appl. Chem.* **1987**, *59*, 61.

(5) Glebov, E. M.; Stepanov, V.; Krishtopa, L. G.; Krasnoperov, L. N. Kinetics of a Diels−Alder Reaction of Isoprene with Maleic Anhydride in Supercritical Carbon Dioxide. 16th International Symposium on Gas Kinetics, Cambridge, U.K., July 23−27 2000; *Abstracts*; 2000; p PE14.

10.1021/jp030232v CCC: $25.00