An Experimental and Theoretical Study of the High Temperature Reactions of Four Butyl Radical Isomers
John B. Randazzo, Ahren W. Jasper, Raghu Sivaramakrishnan, Travis Sikes, Patrick T. Lynch, and Robert S. Tranter
 Phys. Chem. Chem. Phys.

ARRHENIUS FITS, [A (T^n) exp(-Ea/RT)] TO VRC-TST PREDICTIONS FOR THE CAPTURE RATE CONSTANTS FOR THE RADICAL-RADICAL REACTIONS STUDIED IN THIS WORK VALID BETWEEN 300-2000 K.

Units: cal, mol. s, K

1. CH_3 + iso-propyl = iso-butane 3.411E+14 -0.523 -410 ! Fit to within 2%

2. C_2H_5 + iso-propyl = iso-pentane 1.885E+15 -0.871 -356 ! Fit to within 2%

3. CH_3 + sec-Butyl = iso-pentane 1.612E+14 -0.457 -587 ! Fit to within 5%

4. CH_3 + i-Butyl = iso-pentane 2.020E+14 -0.394 -411 ! Fit to within 2%

5. C_2H_5 + n-Butyl = n-Hexane 6.660E+14 -0.621 -447 ! Fit to within 5%

6.   n-propyl + n-propyl = n-Hexane 5.253E+14 -0.713 -458 ! Fit to within 3%

7.   iso-butyl + iso-butyl = 2,5-dimethylhexane 3.561E+15 -1.032 -354 ! Fit to within 8%

8.   sec-butyl + sec-butyl = 3,4-dimethylhexane 1.346E+15 -1.12 -684 !Fit to within 10%

Fit to Geometric Mean Rule (GMR) based rate constants for n-butyl + n-butyl derived from VRC-TST predictions for n-Butyl + C_2H_5 (Reaction 5, present work) and C_2H_5 + C_2H_5 (Ref. 27)

9.   n-butyl+n-butyl = n-octane 3.872E+15 -1.0 -315 !Fit to within 8%

ANALYSIS OF THE DISPROPORTIONATION REACTION IN ISO-BUTYL

Gibian and Corley[1] review the available literature data on the self-reactions of iso-butyl radicals. They conclude that the earlier results from Kraus and Calvert[2] and Metcalfe and Trotman-Dickenson[3] that used di-isobutylketone and isovaleraldehyde respectively as photolysis sources of iso-butyl radicals were influenced by secondary reactions. In particular, increasing yields of iso-butene in these experiments were attributed to facile bimolecular reactions of radicals with the precursor photolyte and as a consequence of this ratios of isobutene/2,5-dimethylhexane could not be solely attributed to the ratio of disproportionation/recombination in the self-reactions of iso-butyl radicals. Terry and Futrell[4] and Slater et al.[5] used a relatively "cleaner" photolysis source, 1,1'-azoisobutane, to generate iso-butyl radicals and measured the yields of isobutene relative to the recombination product, 2, 5-dimethylhexane to obtain

disproportionation/recombination ratios. The studies by Terry and Futrell were performed at room-temperature. On the other hand, the Slater et al. studies span the T-range 296-598 K, but disproportionation/recombination ratios were measured exclusively in 13 experiments over the 368-441 K T-range (see Table 1[5]). An additional 14 experiments over the 350-423 K also measured these ratios but the temperatures at which these ratios were measured are not provided and hence were not used in the present fit. We have chosen the 298 K ratio from Terry and Futrell, the 368-441 K ratios from Slater et al., and the 800 K ratio from the present work with the VRC-TST capture rate prediction (equation 7 above) to obtain disproportionation rate constants. These rate constants are plotted in Fig S1 below. These rate constants are then best-fit to an Arrhenius expression represented by,

10.   iso-butyl + iso-butyl = iso-butene + iso-butane 2.168E+02   3.1   -2762 ! 300-800 K

The observed T-dependence for this disproportionation reaction is in remarkable agreement with the T-dependence predicted in the theoretical calculations by Wu et al.[6] for the disproportionation reaction $CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4$. Interestingly, if the disproportionation/recombination lower temperature ratios were assumed to be constant as concluded by Gibian and Corley and applicable over the present experimental T-Range, that would have resulted in a factor of 4 drop in the disproportionation rate constants from room-T to 800 K.
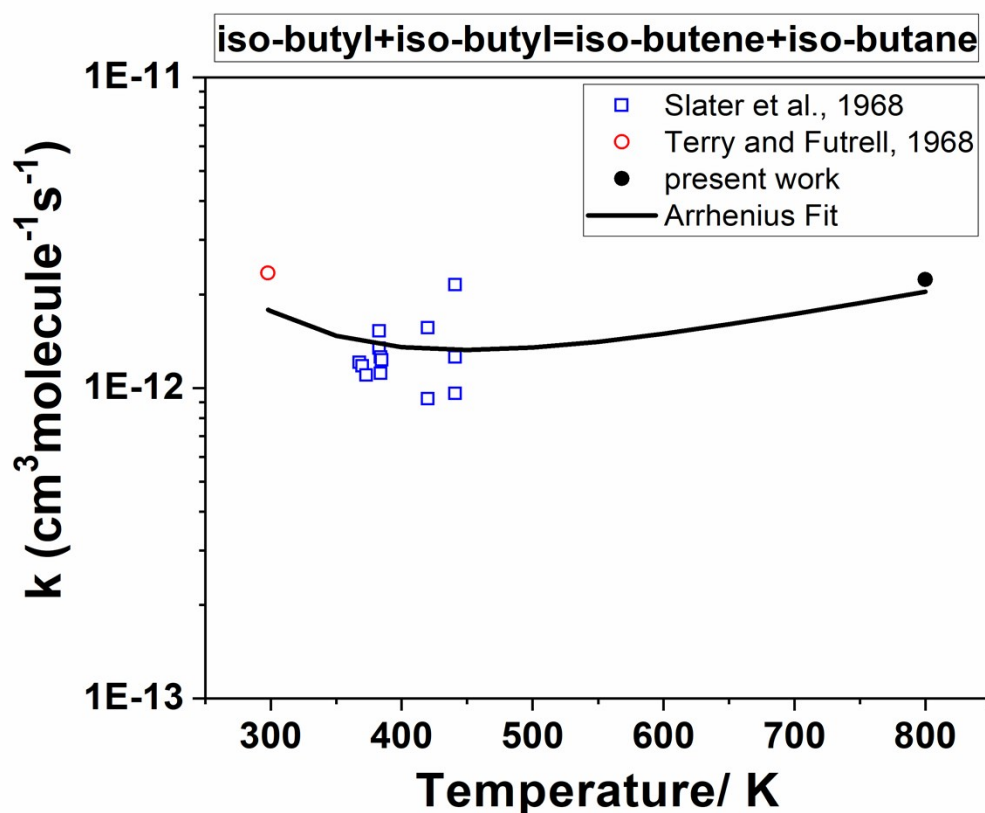

Fig S1: Arrhenius plot for the disproportionation reaction of iso-butyl radicals.

References

1. M. J. Gibian and R. C. Corley, Chem. Rev., 1973, 73, 441–464.

2. J. W. Kraus and J. G. Calvert, J. Amer. Chem. Soc., 1957, 79, 5921-5926.

3. E. L. Metcalfe, A. F. Trotman-Dickenson, J. Chem. Soc., 1960, 5072-5078.

4. J. O. Terry, J. H. Futrell, Can. J. Chem., 1968, 46, 664-665.

5. D. H. Slater, S. S. Collier, J. G. Calvert, J. Amer. Chem. Soc., 1968, 90, 268-273.

6. C. H. Wu, D. B. Magers, L. B. Harding, S. J. Klippenstein, W. D. Allen, J. Chem. Theory Comput., 2020, 16, 1511−1525.