6054 *J. Phys. Chem. A* **1998,** *102,* 6054−6055

Comment on “Inverse Kinetic Isotope Effect in the Reaction of Atomic Chlorine with C_2H_4 and C_2D_4”

E. W. Kaiser* and T. J. Wallington*

Research Laboratory, Mail Drop 3083/SRL, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121-2053

Received: December 19, 1997; In Final Form: April 22, 1998

In their recent paper,[1] Stutz, Ezell, and Finlayson-Pitts presented measurements of the rate constant for the addition reaction $Cl + C_2H_4 + M = ClC_2H_4 + M$ (1) using both absolute (fast flow discharge system, FFDS) and relative rate (RR) techniques. The rate constant at 1 Torr was determined to be $(3.3 \pm 0.6) \times 10^{-13}$ in helium diluent using FFDS and $(2.9 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} using the RR technique with CH_4 as reference. While no individual data are presented, Stutz et al. state that the rate constant of reaction 1 in He is indistinguishable from that in N_2 based on RR data. This result is surprising because N_2 is usually a more efficient third body than He. For example, in O_2 addition to alkyl radicals, N_2 is more efficient than He as a third body by approximately a factor of 2.[2,3] Stutz et al. note that their values of k_1 are significantly smaller than that determined at 1 Torr in our earlier RR experiments[4] (4.8×10^{-13} cm^3 molecule^{-1} s^{-1}). Because the RR technique is capable of precision much better than the 65% discrepancy between our previous measurements and the RR experiments of Stutz, Ezell, and Finlayson-Pitts, we have repeated our measurements in N_2 diluent using both the FTIR and GC methods described in our earlier publication. In addition, we have measured k_1 in helium diluent to provide a better comparison with the absolute measurements of Stutz et al., which were performed in He. Our experiments, therefore, also address the question of the efficiency of He relative to N_2 as a third body in reaction 1.

Briefly, in both GC and FTIR experiments, a mixture of Cl_2, C_2H_4, N_2 (or He), and reference hydrocarbon is irradiated by black-light-blue fluorescent lamps. The decrease in concentration of C_2H_4 and the reference compound is then measured. Detailed descriptions of these experiments have been presented previously.[4]

Experiments were performed over the pressure range 1−5 Torr with the FTIR apparatus using either methyl formate, CH_3OCHO [$k = (1.4 \pm 0.1) \times 10^{-12}$],[5] or CH_3Cl as the reference [$k = (4.8 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}].[6] Typical mixtures had the following initial composition: C_2H_4 = 4−6 mTorr; CH_3OCHO or CH_3Cl = 5−13 mTorr; Cl_2 = 55−130 mTorr; M = balance to desired pressure. The rate constant ratio was determined from a plot of $\ln([C_2H_4]/C_2H_4]_0)$ vs $\ln([\mathrm{ref}]/[\mathrm{ref}]_0)$ for the full set of irradiations on each mixture with the fit forced through the origin. The resulting slope typically had a 2σ error of less than 10%. Figure 1 presents all FTIR data obtained using methyl formate as the reference compound in either He or N_2 diluent. Similar plots were generated using methyl chloride as the reference at pressures of 1 and 2 Torr in N_2. Indistinguishable rate constants were obtained using both reference compounds.

The GC experiments were carried out at 1 and 2 Torr in either He or N_2 diluent using CH_4 as reference [$k = (1.0 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}).[7] The initial mixtures contained 1.3% C_2H_4; 2.6% CH_4, 11−14% Cl_2, and M = balance. The experiments spanned the following C_2H_4 consumption ranges: 50−94% at 1 Torr in He; 85−97% at 2 Torr in He; 64−94% at 1 Torr in N_2; and 95% at 2 Torr in N_2. One experiment was carried out with Cl_2 as the diluent at 1 Torr to determine the third body efficiency of Cl_2 relative to N_2 since both FTIR and GC experiments used appreciable Cl_2 mole fractions (10−15%). The measured rate constant increased by 30% in the pure Cl_2 mixture relative to a mixture with 11% Cl_2 in N_2. This indicates that Cl_2 is approximately 35% more efficient as a third body than N_2 and that the presence of 11% Cl_2 in a mixture would increase the measured rate constant by 4% over that expected in pure N_2, an effect less than the experimental data scatter, and no correction has been made. The FTIR experiments typically had 2−4 times less hydrocarbon present in the mixture than did the GC measurements. The fact that identical rate constants were obtained by the two techniques indicates that the small amounts of hydrocarbons in the mixtures do not affect the measured rate constants to within experimental error. As additional verification, one GC experiment was performed at 1 Torr (N_2) with the hydrocarbon concentrations increased by a factor of 3. The rate constant was indistinguishable from those determined at lower HC concentration to within the 10% uncertainty.

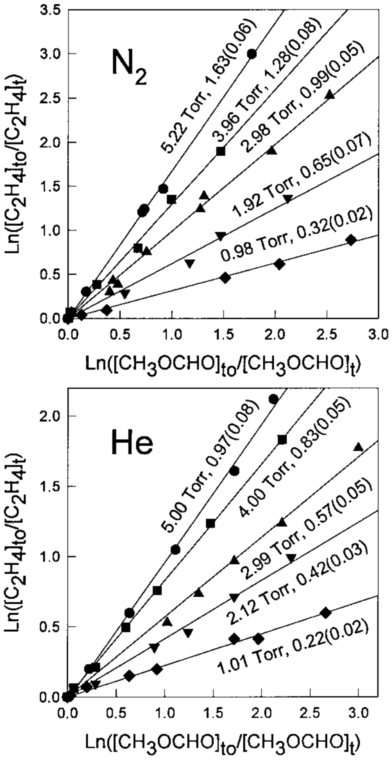

Figure 1. FTIR relative rate experiments using methyl formate as reference compound at 1−5 Torr total pressure in N_2 or He diluent. The labels for each set of experimental data present the pressure and the slope of the line [$=k_1/k_{\mathrm{ref}}$]. The number in parentheses represents two statistical standard deviations of the slope.

The results of our current experiments are presented in Figure 2 along with the measured rate constants in the 1−5 Torr range determined during our previous experiments in N_2 diluent.[4] The measured rate constants for different initial reactant concentrations, percentages of consumption, reference compound, and

S1089-5639(98)00578-7 CCC: $15.00

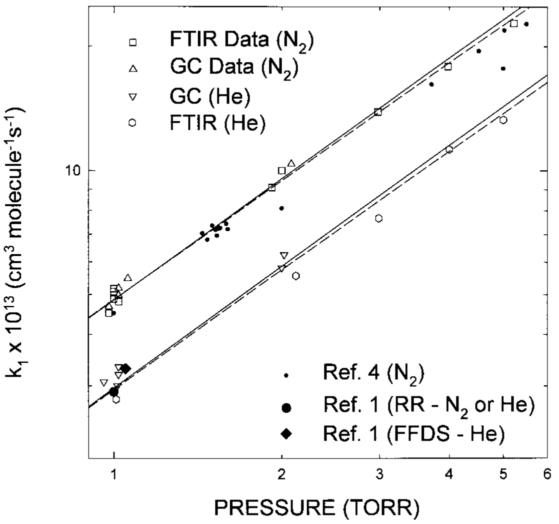

Figure 2. Relative rate determination of the value of k_1 in these experiments using both FTIR and GC methods in He or N_2 diluent at pressures between 1 and 5 Torr. Also included are our previous data from ref 4 and data from Stutz et al. Lines represent Troe fits to the current data as discussed in the text.

reactors with different S/V ratio are identical to within the data scatter. This demonstrates that neither secondary nor surface reactions impact the results significantly. The current results agree well with our previous measurements. The rate constant at 1 Torr in N_2 determined by averaging both GC and FTIR data ($k_1 = (4.97 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, in which the error represents 2σ of the mean of the nine measurements) is approximately 70% higher than the RR determination of Stutz et al., which is also presented in Figure 2.

On the basis of our results in He + Cl_2 mixtures and the efficiency of Cl_2 presented above, we estimate that the efficiency of He as a third body is approximately 60% of that of N_2. The rate constants determined in a He + Cl_2 mixture will be somewhat higher than in pure He. Therefore, the He rate constants in Figure 2 have been corrected for the larger third body efficiency of Cl_2, resulting in a value appropriate for pure He. This small correction constitutes a 12% reduction from the values measured in the He + Cl_2 mixture at both 1 and 2 Torr for the GC experiments. In the FTIR measurements, the reduction is 10% at 1 Torr, decreasing to 2% at 5 Torr. The corrected rate constants determined for pure He diluent are significantly lower than those in N_2 in our experiments, contrary to the observation of Stutz et al. Our value of k_1 at 1 Torr in He ($=(3.0 \pm 0.3) \times 10^{-13}$) agrees with that measured by Stutz et al. using the FFDS technique in He ($(3.3 \pm 0.6) \times 10^{-13}$).

The lines in Figure 2 are fits using the Troe formalism.[4] The rate constants in the high-pressure limit are those determined in ref 4 for N_2: 3.2×10^{-10} cm^3 molecule^{-1} s^{-1} using $F_{\text{cent}} = 0.6$ and 5.7×10^{-10} cm^3 molecule^{-1} s^{-1} using $F_{\text{cent}} = 0.4$. In N_2, the low-pressure rate constants obtained from these two values of F_{cent} are 1.85×10^{-29} and 1.65×10^{-29} cm^6 molecule^{-2} s^{-1} for 0.4 (dashed line) and 0.6 (solid line), respectively. These values of k_0 are approximately 15% larger than quoted in ref 4 because we have chosen to fit the data above 1 Torr without the small y-axis intercept used in that reference. As stated in ref 4, this apparent nonzero intercept was likely a result of a small (0.1 Torr) pressure measurement uncertainty. For the current experiments, we have recalibrated our pressure measuring devices, and any uncertainty is now less than 0.02 Torr. The lines through the He data are obtained using the following rate constants: $k_\infty = 3.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $F_{\text{cent}} = 0.6$, $k_0 = 1.0 \times 10^{-29}$ cm^6 molecule^{-2} s^{-1} (solid line); $k_\infty = 5.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $F_{\text{cent}} = 0.4$, $k_0 = 1.11 \times 10^{-29}$ cm^6 molecule^{-2} s^{-1} (dashed line).

In conclusion, our new measurements of k_1 in N_2 are in excellent agreement with previous work at Ford.[4] Our current experiments demonstrate that He is a less efficient third body than N_2 by a factor of approximately 0.6. The new results in He at 1 Torr agree with the results obtained by Stutz et al. in an absolute rate experiment (FFDS) with He diluent. In N_2 at 1 Torr, however, our measurement remains 70% larger than that determined in the relative rate experiments of Stutz et al., a discrepancy substantially larger than the combined experimental uncertainties.

References and Notes

(1) Stutz, J.; Ezell, M. J.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **1997**, *101*, 9187.

(2) Kaiser, E. W.; Lorkovic, I. M.; Wallington, T. J. *J. Phys. Chem.* **1990**, *94*, 3352.

(3) Kaiser, E. W. *J. Phys. Chem.* **1993**, *97*, 11681.

(4) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 4111.

(5) Wallington, T. J.; Hurley, M. D.; Ball, J. C. *Chem. Phys. Lett.* **1993**, *211*, 41.

(6) Wallington, T. J.; Andino, J. M.; Ball, J. C.; Japar, S. M. *J. Atmos. Chem.* **1990**, *10*, 301.

(7) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. Jet Propulsion Laboratory Publication 97-4, Pasadena, CA, 1997.