

# Selective Free Radical Reactions using Supercritical Carbon Dioxide

Philip J. Cormier, Ryan M. Clarke, Ryan M. L. McFadden, and Khashayar Ghandi\*

Department of Chemistry and Biochemistry, Mount Allison University, 63C York Street, Sackville, New Brunswick E4L 1G8, Canada

**S** Supporting Information

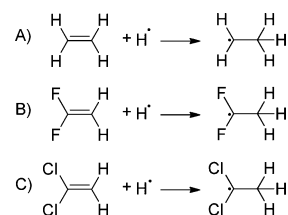
**ABSTRACT:** We report herein a means to modify the reactivity of alkenes, and particularly to modify their selectivity toward reactions with nonpolar reactants (e.g., nonpolar free radicals) in supercritical carbon dioxide near the critical point. Rate constants for free radical addition of the light hydrogen isotope muonium to ethylene, vinylidene fluoride, and vinylidene chloride in supercritical carbon dioxide are compared over a range of pressures and temperatures. Near carbon dioxide's critical point, the addition to ethylene exhibits critical speeding up, while the halogenated analogues display critical slowing. This suggests that supercritical carbon dioxide as a solvent may be used to tune alkene chemistry in near-critical conditions.

Supercritical carbon dioxide (scCO<sub>2</sub>) [critical point: 31.1 °C and 73.8 bar] has been touted as an alternative to conventional organic solvents, due to its low flammability, effective recyclability, and reduced handling risk.<sup>1</sup> scCO<sub>2</sub> lends itself to diverse applications; it can be used to impregnate polymers with organometallic compounds,<sup>2</sup> increase the selectivity of certain catalysts,<sup>3</sup> or even act as a medium for electrochemical polymerizations.<sup>4</sup> Moreover, industry has found scCO<sub>2</sub> to be an excellent solvent for polymer synthesis and modification, e.g. polyethylene formation,<sup>5,6</sup> ring-opening metathesis,<sup>7</sup> or halogenation of polymers.<sup>8,9</sup>

Alkenes make an excellent feedstock for the petrochemical industry because they participate in a wide range of reactions.<sup>10</sup> The physical properties of scCO<sub>2</sub> may be tuned thermodynamically, i.e., small changes to temperature or pressure, especially near its critical point, can give rise to significant changes in the fluid's properties.<sup>1</sup> This opens the possibility of using a solvent that can be tailored to control reaction kinetics. Thus, we propose the following: is it possible to control reactivity or selectivity of alkenes using this property?

To address this question, we studied arguably the least selective of all alkene reactions: free radical additions. If selectivity can be shown for these reactions, it is likely that there will be more selectivity toward other reactions involving alkenes in scCO<sub>2</sub>. Such a study requires an understanding of the mutual effect of temperature and pressure on reaction rates. However, the current understanding of a dual thermodynamic dependence for free radical additions is unfortunately limited. Normally this information is derived from product analysis and reaction modeling,<sup>11,12</sup> where it is assumed that propagation rate constants are not influenced by pressure.<sup>13</sup> Thus, our inquiry serves additionally to augment our understanding of such phenomena.

The simplest free radical reactions are those involving atomic hydrogen. Such reactions are fundamental to understanding of reaction rate theories.<sup>14</sup> However, more conventional techniques (e.g., flash photolysis or pulse radiolysis)<sup>15</sup> cannot be used to probe H-atom reactions in scCO<sub>2</sub>, as there is no intrinsic proton source, and using additives could perturb the system and alter the fundamental properties of scCO<sub>2</sub>. To overcome this, we employ the light hydrogen radioisotope muonium (Mu), which has been shown to be unreactive with CO<sub>2</sub> over a large range of temperatures and pressures.<sup>16</sup> Mu is an atom, with a positive muon ( $\mu^+$ ,  $\sim 2.2 \mu\text{s}$  lifetime, mass  $\sim 0.11 \text{ u}$ ) as the nucleus. In particular we have studied Mu reaction kinetics with ethylene (ET), vinylidene fluoride (VDF), and vinylidene chloride (VDC). Figure 1 shows analogous H-atom reactions.



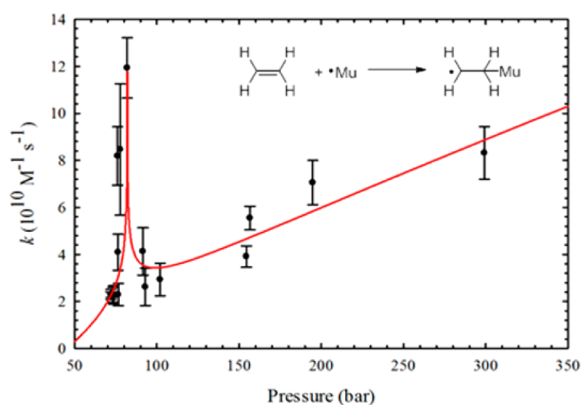
**Figure 1.** Reaction schemes for (A) H addition to ET, (B) H addition to VDF, and (C) H addition to VDC. Several other radical transients are possible, but only the most kinetically favored product is shown.

In TF- $\mu$ SR experiments (see Supporting Information) if Mu undergoes a chemical reaction that places the muons in a different magnetic environment, then the resulting spin dephasing manifests as decay in the Mu precession signal. Mu kinetics is inferred from this decay, after correcting for the muon radioactive decay. This method allows for a direct measurement of Mu rate constants, eliminating the need to make approximations or assumptions required in traditional product analysis methods. Full details of our method and set up may be found in the Supporting Information and in our previous work.<sup>17–19</sup> Rate coefficients were determined for a wide range of temperatures, pressures, and densities. All studied samples were oxygen-free.

For reaction of Mu with ET the product corresponds to Mu addition.<sup>17</sup> There is no reaction between CO<sub>2</sub> and ethyl radical, which means CO<sub>2</sub> combined with simple alkenes could not be used as a feedstock in free radical chemistry.<sup>20</sup> Figure 2 displays the pressure dependence of rate constants for Mu + ET in CO<sub>2</sub> at  $T = 305 \text{ K}$ . A general increase in the rate of addition is observed as pressure increases. At densities close to the critical

Received: August 17, 2013

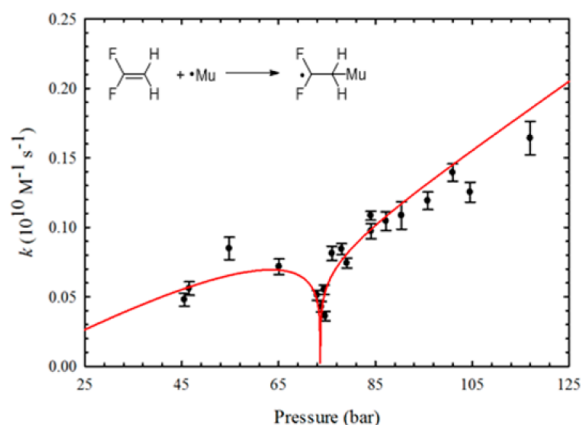
Published: January 29, 2014



**Figure 2.** Rate constants for Mu + ET in CO<sub>2</sub> at  $T = 305$  K. The solid line is a fit to eq 1.

density, where isothermal compressibility reaches a maximum, the rate constant increases sharply to a local maximum. This is known as critical speeding up. Though this phenomenon has been postulated,<sup>21,22</sup> to the best of our knowledge this is the first reported example of critical speeding up for reactions in any supercritical fluid. However, critical speeding up has been observed for S<sub>N</sub>1 reactions at their respective consolute points in a binary liquid system.<sup>23</sup>

The Mu + VDF reaction in CO<sub>2</sub> has a single product.<sup>18</sup> Part of the data from our recent study<sup>19</sup> on the density dependence of Mu + VDF kinetics is shown in Figure 3. A general increase



**Figure 3.** Rate constants for Mu + VDF in CO<sub>2</sub> at  $T = 305$  K.<sup>19</sup> The solid line is a fit to eq 1.

in rate constants with increasing pressure is observed, but a sharp decrease to a local minimum is observed (i.e., critical slowing down of the reaction) at a pressure close to a maximum in CO<sub>2</sub>'s isothermal compressibility. This behavior, along with the thermodynamic mapping of rate constants, and the determination of optimal thermal parameters for Mu to VDF addition rate tuning were previously reported by our group.<sup>19</sup>

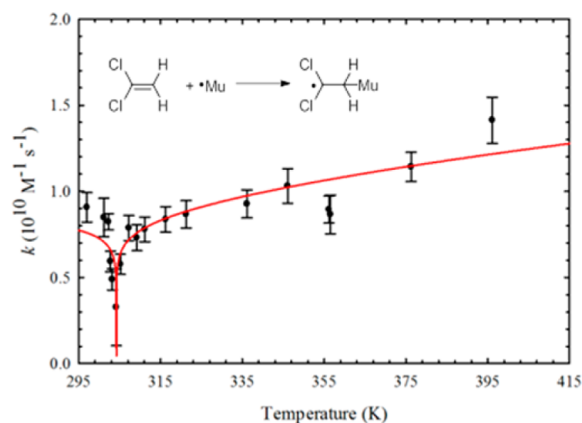
Both cases of Mu addition to ET and VDF show significant rate dependences on pressure and extreme sensitivity to changes in pressure near the critical pressure. The minimum and maximum in both rate constants can be attributed to density inhomogeneity in scCO<sub>2</sub> near the critical point causing critical slowing or speeding up.<sup>19,23</sup> Also, the results show that the addition of halogen functional groups to ET can drastically change the kinetics in scCO<sub>2</sub>. Rate constants for radical addition are fitted to a general empirical expression

$$k = A + \alpha P \left| \frac{P - P_c}{P_c} \right|^\gamma \quad (1)$$

where  $k$  is the rate constant,  $P$  is the pressure,  $A$  is a constant,  $\alpha$  is a scaling factor,  $P_c$  is the pressure where compressibility reaches a maximum, and  $\gamma$  is the critical exponent. The pressure dependence of many reactions is linear. We follow this general formulation, but adopt an additional "divergence" factor,  $|(P - P_c)/P_c|^\gamma$ , to account for the departure from linearity near  $P_c$ . The sign of  $\gamma$  is indicative of either critical slowing down ( $\gamma > 0$ ), speeding up ( $\gamma < 0$ ), or insensitivity to critical phenomena ( $\gamma = 0$ ). Far from  $P_c$  in the low-pressure limit, our expression approaches a constant value representative of the low-pressure gas phase rate constant.

In the low pressure limit (i.e., in the gas phase) Mu addition to ET is dominated by tunneling; the kinetic isotope effect ranges from  $k_{\text{Mu}}/k_{\text{H}} \approx 30$  at  $T = 165$  K to  $k_{\text{Mu}}/k_{\text{H}} \approx 2.8$  at  $T = 500$  K.<sup>24</sup> Therefore the rate of reaction of H atoms is expected to be slightly smaller than that of Mu within our examined range of temperatures and pressures. In the high-pressure limit, our "divergence" term becomes negligible within the realm of pressures examined experimentally. It should be stated though that our expression is primarily concerned with the description of  $k$  as  $P \rightarrow P_c$ , and it should not be used as an accurate means of predicting high- or low-pressure limit rate constants.

As a natural progression from ET and VDF, our third investigated reaction was Mu + VDC in CO<sub>2</sub>. Overall the rate constants for addition to ET are the largest followed by the addition to the VDC. The smallest rate constants are for addition to VDF. Our results show that at temperatures near CO<sub>2</sub>'s critical temperature ( $T_c$ ), this reaction exhibits critical slowing down. Figure 4 shows the temperature dependence of



**Figure 4.** Rate constants for the Mu + VDC reaction in CO<sub>2</sub> ( $\rho \approx 0.2$  g cm<sup>-3</sup>). The solid line is a fit to eq 2.

rate constants for Mu + VDC in CO<sub>2</sub> at  $\rho \approx 0.2$  g cm<sup>-3</sup>. Near  $T_c$ , these rate constants can be fit to a modified Arrhenius expression

$$k = A \left| \frac{T - T_c}{T_c} \right|^\gamma e^{-E_a/RT} \quad (2)$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the ideal gas constant,  $T$  is the absolute temperature,  $T_c$  is the critical temperature, and  $\gamma$  is the critical exponent. It should be noted that this expression only holds for  $T \sim T_c$ . For temperatures far from  $T_c$ , an unmodified Arrhenius

expression (i.e.,  $\gamma = 0$  for  $T \gg T_c$  and  $T \ll T_c$ ) suitably describes the temperature dependence of these rate constants.

Near the critical point, the system becomes inhomogeneous with fluctuating high and low-density regimes. Since an oscillating single exponential decay best describes the time evolution in our experiments, the solvent fluctuations are fast on the microsecond time scale of the measurement, or alternatively, both reactants average between these two environments by fast diffusion, and therefore the kinetics may be treated as homogeneous.

When there is a negative critical exponent the reactants reside mainly in the low-density region (both reactants have intermolecular interactions with solvent molecules that are smaller than the solvent–solvent interactions), and therefore the average rate increases. This increase in rate is either due to an increase in the rate constant or an increased concentration of the reactants.

For TF- $\mu$ SR experiments using a continuous beam, such as those at TRIUMF in Canada, where these experiments were performed, there is only one Mu atom at any time during the experiment, meaning that either the rate constant or the concentration of the alkene is increased. If the latter is the case, this means that on average (over time) the alkene prefers to cluster in the same environment as Mu, and therefore, on average, Mu encounters a larger concentration of alkenes than at conditions away from the critical point.

This would mean on average both Mu and the alkene prefer to be in the low density region, while the opposite effect is expected for substituted alkenes where a positive critical exponent is observed. Here the Mu would be found in the low density region and the halogenated alkenes in the high density regions. The other possibility is having much faster than microsecond fluctuations of the concentration and therefore the same average concentration as far away from resonance and an associated resonance in the rate constants. In effect and from a practical point of view, both would lead to a resonance in the rate of reaction (i.e., concentration multiplied by rate constant).

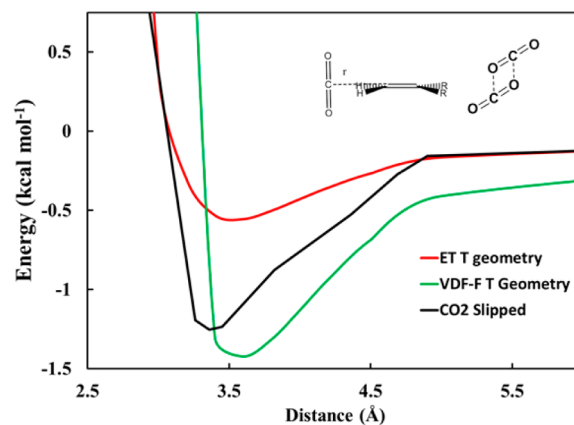
CO<sub>2</sub> is a nonpolar medium. It has a large quadrupole moment, and its density can be appreciably changed as a function of temperature and pressure. At its critical pressure, CO<sub>2</sub>'s compressibility is maximized, and small changes to thermal parameters can lead to large changes in its local density. In effect, the closer the system temperature and pressure to their critical values, the greater the effect of local density enhancement.<sup>25</sup> Raman studies have shown that in near-critical conditions, neat CO<sub>2</sub> exhibits local density enhancement between (CO<sub>2</sub>)<sub>2</sub> dimers.<sup>26</sup> This is where we observe the most dramatic difference in rate coefficients between our studied olefins.

Halogenated olefins such as VDF and VDC are more soluble in scCO<sub>2</sub> than hydrocarbons.<sup>27</sup> Molecular dynamics simulations involving *cis*- and *trans*-1,2 dichloroethylene (DCE) have shown that the factors that contribute to the local density enhancement are greater with a mixture of CO<sub>2</sub> and DCE than pure CO<sub>2</sub> and that the *cis* and *trans* geometry of DCE had little effect on this.<sup>28</sup>

Although such simulations can provide angle-dependent pair correlations (among others), such calculations are beyond the scope of the present work. Indeed, such calculations require the use of very accurate force fields, which are not currently available for VDC, VDF, and ET.<sup>29</sup> Instead, we have performed preliminary DFT calculations at limited configurations of CO<sub>2</sub> with ET or VDF to investigate their possible intermolecular

interactions. Though such calculations are unlikely to provide quantitative accuracy, we believe they have the ability to identify useful qualitative features of the potential energy surfaces involving these species.

Our quantum calculations,<sup>30</sup> using the B3LYP hybrid density functional<sup>31</sup> and a 6-311++G(2df,p) split-valence basis set, have shown that the interaction of CO<sub>2</sub> and VDF is more attractive than the interaction between CO<sub>2</sub>–CO<sub>2</sub> (Figure 5).



**Figure 5.** Energy of interaction of ET–CO<sub>2</sub> at T geometry, CO<sub>2</sub>–CO<sub>2</sub> in slipped, and VDF–CO<sub>2</sub> in T geometry.

The interaction energy is defined as  $E_{AB} - E_A - E_B$ , where  $E_{AB}$  is the energy of the interacting species at a distance  $r$  and  $E_A$  and  $E_B$  are the energy of the two species separated to infinity. The interaction energies were corrected for basis set superposition errors (BSSEs), although the maximum BSSEs were 10%. Using the format defined by Bukowski, there are two geometries for CO<sub>2</sub> that give a local minimum: T-shaped and slipped parallel (see Figure S2 in Supporting Information).<sup>32</sup> Our values were close to those calculated by Tsuzuki et al.<sup>33</sup> Our slipped parallel and T-shape forms have energies of  $-1.26$  and  $-1.10$  kcal/mol, respectively, whereas the Tsuzuki interaction energy is  $-1.29$  and  $-1.07$  kcal/mol for equivalent geometries and are in good agreement with those of Bukowski et al.<sup>32</sup> The interaction energy between ET and CO<sub>2</sub> and VDF and CO<sub>2</sub> was also investigated. In this case,  $r$  is defined by the distance from the terminal C atom in either ET or VDF and the central C atom in CO<sub>2</sub>. The two lowest local minimum geometries were one in which CO<sub>2</sub> and ET (or VDF) are in a slipped geometry (see Figures S1, S2, and S4 in the Supporting Information), and one where CO<sub>2</sub> is at 90 degrees to the terminal carbon of ET (or VDF), see Figure 5.

Within the limits of our calculations (a small number of relative configurations) for ET–CO<sub>2</sub>, the overall energy is less attractive than CO<sub>2</sub>–CO<sub>2</sub> interactions. In effect, the attractive order of molecular interaction is likely to be as follows: VDF–CO<sub>2</sub> > CO<sub>2</sub>–CO<sub>2</sub> > ET–CO<sub>2</sub>  $\gg$  H–CO<sub>2</sub>, as the H-atom and CO<sub>2</sub> show very weak attraction.<sup>34</sup> This suggests that the critical speeding up of the H-atom addition to ethylene may be due to the weaker interactions between CO<sub>2</sub> and ET, compared to CO<sub>2</sub> and CO<sub>2</sub>. In the same way, we attribute the phenomenon of critical slowing of VDF to local density enhancements at the critical point where CO<sub>2</sub> isolates the VDF (which is CO<sub>2</sub>-philic) from H (CO<sub>2</sub>-phobic). This would put the ET and the H-atom in “voids,” increasing the probability of reaction, leading to an increased rate. Conversely, VDF would be in

solvent shells reducing the probability of the radical addition near the critical point.

As noted, a quantitative model of interaction energy is beyond the scope of this mostly experimental work. More extensive calculations that include configurational sampling and higher levels of theory would undoubtedly prove very useful in this regard. Nevertheless, our present DFT calculations serve as a qualitative discussion of a potential reason behind our experimental observations.

Mu addition reactions are analogous to propagation steps in free radical polymerization, where the structure of the resulting polymer chain is determined from the ratio of rate constants for competing reactions.<sup>35</sup> In Figure S3 (Supporting Information), we reported the ratio of rate constants for Mu addition to ET and VDF ( $k_{ET}/k_{VDF}$ ). The ratio for these rate constants changes by more than 2 orders of magnitude close to  $P_c$ . This demonstrates the reaction-tuning ability of CO<sub>2</sub> with a small change in pressure close to critical point.

Our results can, in principle, be applied to reactions involving an alkene and another reactive partner. This, for example, could influence the selectivity of Diels–Alder reactions, the oxidation of alkenes, and, we believe, it can open up new areas of chemistry: (1) the use of near-critical CO<sub>2</sub> to selectively drive reactions and (2) the engineering of critically controllable reactions by considering the intermolecular interactions of reactants and the reaction medium.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details are available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

kgbandi@mta.ca

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We would like to thank the staff at the TRIUMF CMMS facility for their technical expertise and all the support they gave to us. We would also like to thank the Natural Sciences and Engineering Research Council of Canada for funding. We would also like to thank Dr. Greg Sandala in our group for valuable discussions.

## ■ REFERENCES

- (1) Jessop, P. G.; Jessop, D. A.; Fu, D.; Phan, L. *Green Chem.* **2012**, *14*, 1245–1259.
- (2) Clarke, M. J.; Cooper, A. I.; Howdle, S. M.; Poliakoff, M. *J. Am. Chem. Soc.* **2000**, *122*, 2523–2531.
- (3) Kainz, S.; Brinkmann, A.; Pfaltz, A. *J. Am. Chem. Soc.* **1999**, *121*, 6421–6429.
- (4) Anderson, P. E.; Badlani, R. N.; Mayer, J.; Mabrouk, P. A. *J. Am. Chem. Soc.* **2002**, *124*, 10284–10285.
- (5) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543–563.
- (6) Cooper, A. I. *J. Mater. Chem.* **2000**, *10*, 207–234.
- (7) Fürstner, A.; Ackermann, L.; Beck, K.; Hori, H.; Koch, D.; Langemann, K.; Liebl, M.; Six, C.; Leitner, W. *J. Am. Chem. Soc.* **2001**, *123*, 9000–9006.
- (8) Wood, C. D.; Cooper, A. I.; DeSimone, J. M. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 325–331.

- (9) Du, L.; Kelly, J. Y.; Roberts, G. W.; DeSimone, J. M. *J. Supercrit. Fluids* **2009**, *47*, 447–457.
- (10) Wang, Z.; Yang, Y. J.; Dong, Q. Z.; Hu, C. P. *J. Appl. Polym. Sci.* **2008**, *110*, 468–474.
- (11) Liu, T.; DeSimone, J. M.; Roberts, G. W. *Chem. Eng. Sci.* **2006**, *61*, 3129–3139.
- (12) Costa, L. I.; Storti, G.; Morbidelli, M.; Ferro, L.; Galia, A.; Scialdone, O.; Filardo, G. *Macromol. React. Eng.* **2012**, *6*, 24–44.
- (13) Beuermann, S.; Buback, M. Kinetics of free-radical polymerization in homogeneous phase of supercritical carbon dioxide. In *Supercritical Carbon Dioxide: In Polymer Reaction Engineering*; Kemmere, F. M., Meyer, T., Eds; Wiley: Weinheim, 2006; pp 55–80.
- (14) Fleming, D. G.; Arseneau, D. J.; Sukhorukov, O.; Brewer, J. H.; Mielke, S. L.; Shatz, G. C.; Garrett, B. C.; Peterson, K. A.; Truhlar, D. G. *Science* **2011**, *331*, 448–450.
- (15) Lin, M.; Katsumura, Y.; Muroya, Y.; He, H.; Wu, G.; Han, Z.; Miyazaki, T.; Kudo, H. *J. Phys. Chem.* **2004**, *108*, 8287–8295.
- (16) Ghandi, K.; Bridges, M. D.; Arseneau, D. J.; Fleming, D. G. *J. Phys. Chem. A* **2004**, *108*, 11613–11625.
- (17) Cormier, P.; Arseneau, D. J.; Brodovitch, J. C.; Lauzon, J. M.; Taylor, B. A.; Ghandi, K. *J. Phys. Chem. A* **2008**, *112*, 4593–4600.
- (18) Satija, P.; McFadden, R. M. L.; Cormier, P.; Ghandi, K. *Int. Rev. Chem. Eng.* **2011**, *3*, 542–549.
- (19) Ghandi, K.; McFadden, R. M. L.; Cormier, P. J.; Satija, P.; Smith, M. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8502–8505.
- (20) Chateauneuf, J. E.; Zhang, J.; Foote, J.; Brink, J.; Perkovic, M. W. *Adv. Environ. Res.* **2002**, *6*, 487–493.
- (21) Procaccia, I.; Gitterman, M. *Phys. Rev. Lett.* **1981**, *46*, 1163–1165.
- (22) Gitterman, M. *Physica A* **2009**, *388*, 1046–1056.
- (23) Kim, W. Y.; Baird, J. K. *J. Phys. Chem. A* **2003**, *107*, 8435–8443.
- (24) Garner, D. M.; Fleming, D. G.; Arseneau, D. J.; Senba, M.; Reid, I. D.; Milkula, R. J. *J. Chem. Phys.* **1990**, *30*, 1732–1740.
- (25) Tucker, S. C. *Chem. Rev.* **1999**, *99*, 391–418.
- (26) Cabco, M. I.; Longelin, S.; Danten, Y.; Besnard, M. *J. Phys. Chem. A* **2007**, *111*, 12966–12971.
- (27) Raveendran, P.; Ikushima, Y.; Wallen, S. L. *Acc. Chem. Res.* **2005**, *38*, 478–481.
- (28) Dellis, D.; Skarmoutsos, I.; Samios, J. *J. Phys. Chem. B* **2001**, *115*, 12098–12107.
- (29) For this reason, our current computational efforts involve the use of DFT based ab initio MD simulations (Car–Parrinello) to describe the intermolecular interactions of CO<sub>2</sub>, ET, and VDF. Such an approach obviates the requirement for accurate force field development. We will report the results of these investigations in a future publication.
- (30) Frisch, M. J.; et al. *Gaussian 09*, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- (31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (32) Bukowski, R.; Sadlej, J.; Jeziorski, B.; Jankowski, P.; Szalewicz, K.; Kucharski, S. A.; Williams, H. L.; Rice, B. M. *J. Chem. Phys.* **1999**, *110*, 3785–3803.
- (33) Tsuzuki, S.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Chem. Phys.* **1998**, *109*, 2169–2175.
- (34) Lukeš, V.; Ilčin, M.; Laurinc, V.; Biskupič, S. *Chem. Phys.* **2003**, *290*, 93–100.
- (35) Yamada, B.; Zetterlund, P. B.; Sato, E. *Prog. Polym. Sci.* **2006**, *31*, 835–877.