Supplementary Material (ESI) for *PCCP*

Competition between Birch reduction and fluorine abstraction in reactions of hydrated electrons with the isomers of di- and trifluorobenzene

Robert F. Höckendorf, Petru O. Balaj, and Martin K. Beyer, Institut für Physikalische Chemie, Christian-Albrechts-Universitä zu Kiel, Olshausenstrasse 40, 24098 Kiel, Germany, e-mail: beyer@phc.uni-kiel.de

Electronic Supplementary Information

Full reference 67:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

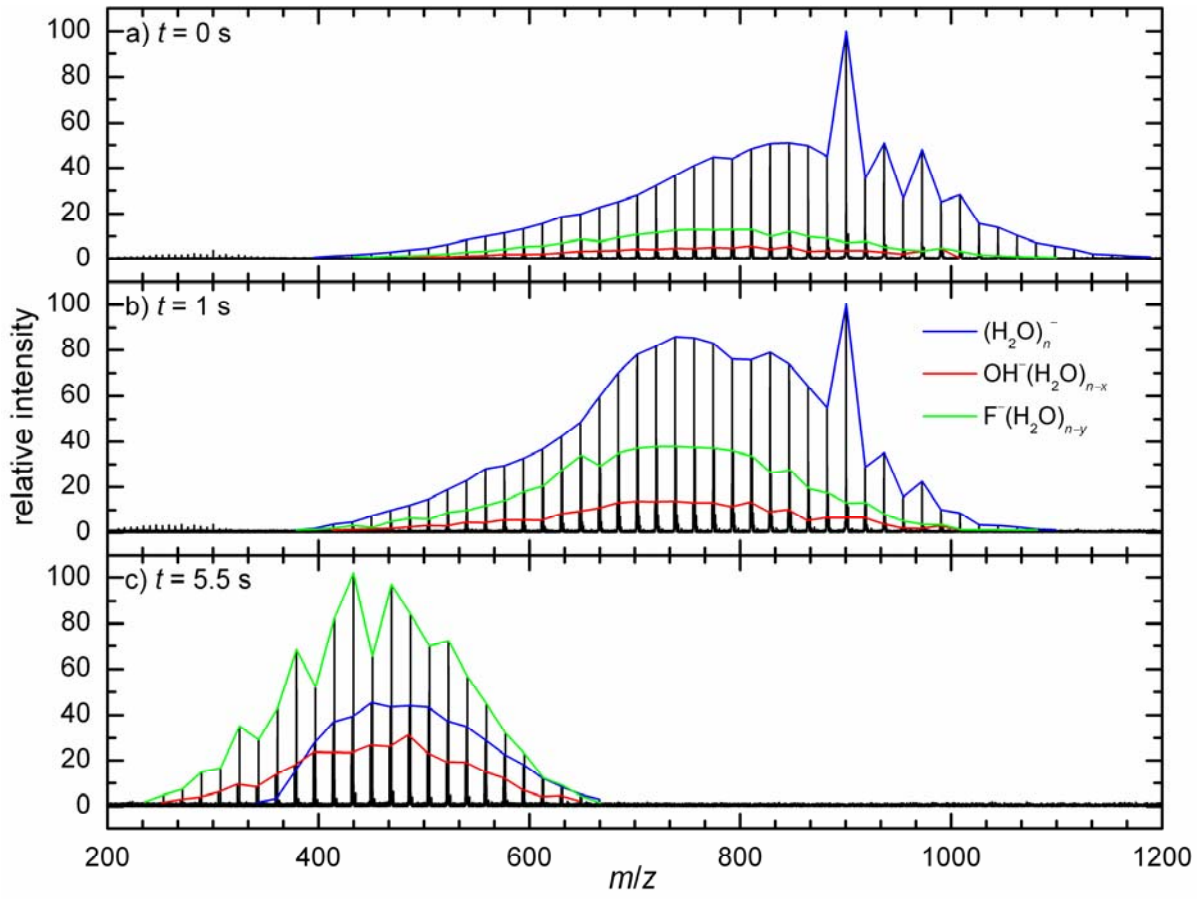

Figure S1

Mass spectra of the reaction of hydrated electrons towards 1,2,3-TFB with increasing reaction delay. The colored lines show the envelope of reactant and product clusters with different size. 1,2,3-TFB preferentially reacts via fluorine abstraction, contrary to 1,2-DFB shown in Fig. 1, which undergoes Birch reduction exclusively.

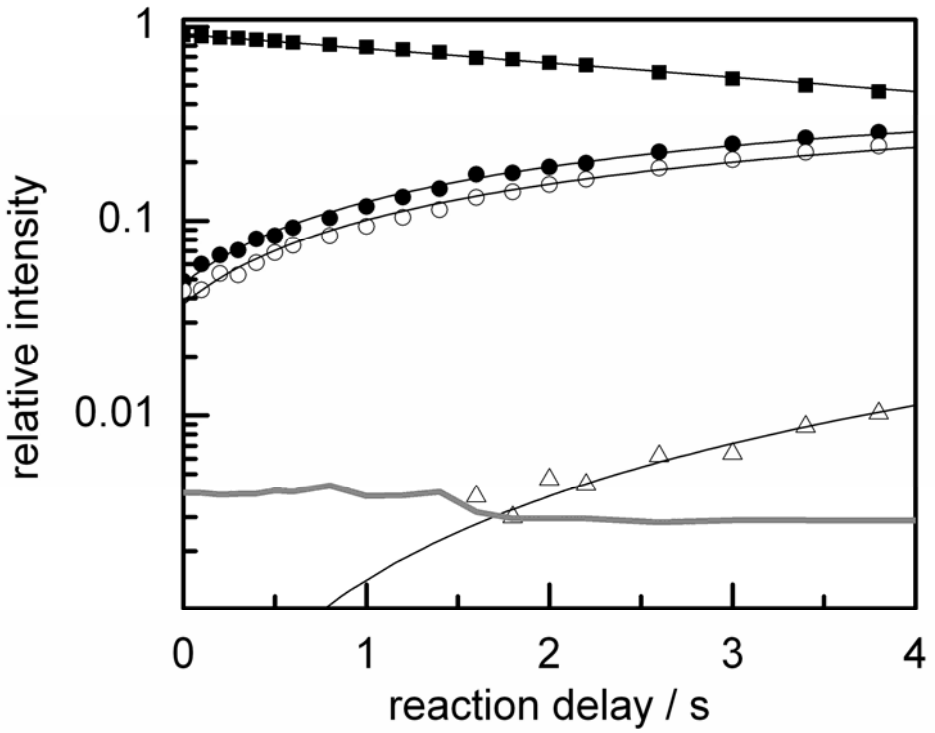

Figure S2

Kinetic fit for the reactions of hydrated electrons with 1,3,5-TFB at a constant reactant pressure of $p = 5.5\times10^{-8}$ mbar. $H_2O_n^-$(■), $OH^-(H_2O)_n$ (●), $F^-(H_2O)_n$ (○) and $FCCH^-(H_2O)_n$ (△). The assignment of $FCCH^-(H_2O)_n$ is based on absolute mass measurement at long reaction delay and low reactant gas pressure. The intensity of $FCCH^-(H_2O)_n$ is fitted as a secondary product. Treatment as a primary product leads to significant deviations.

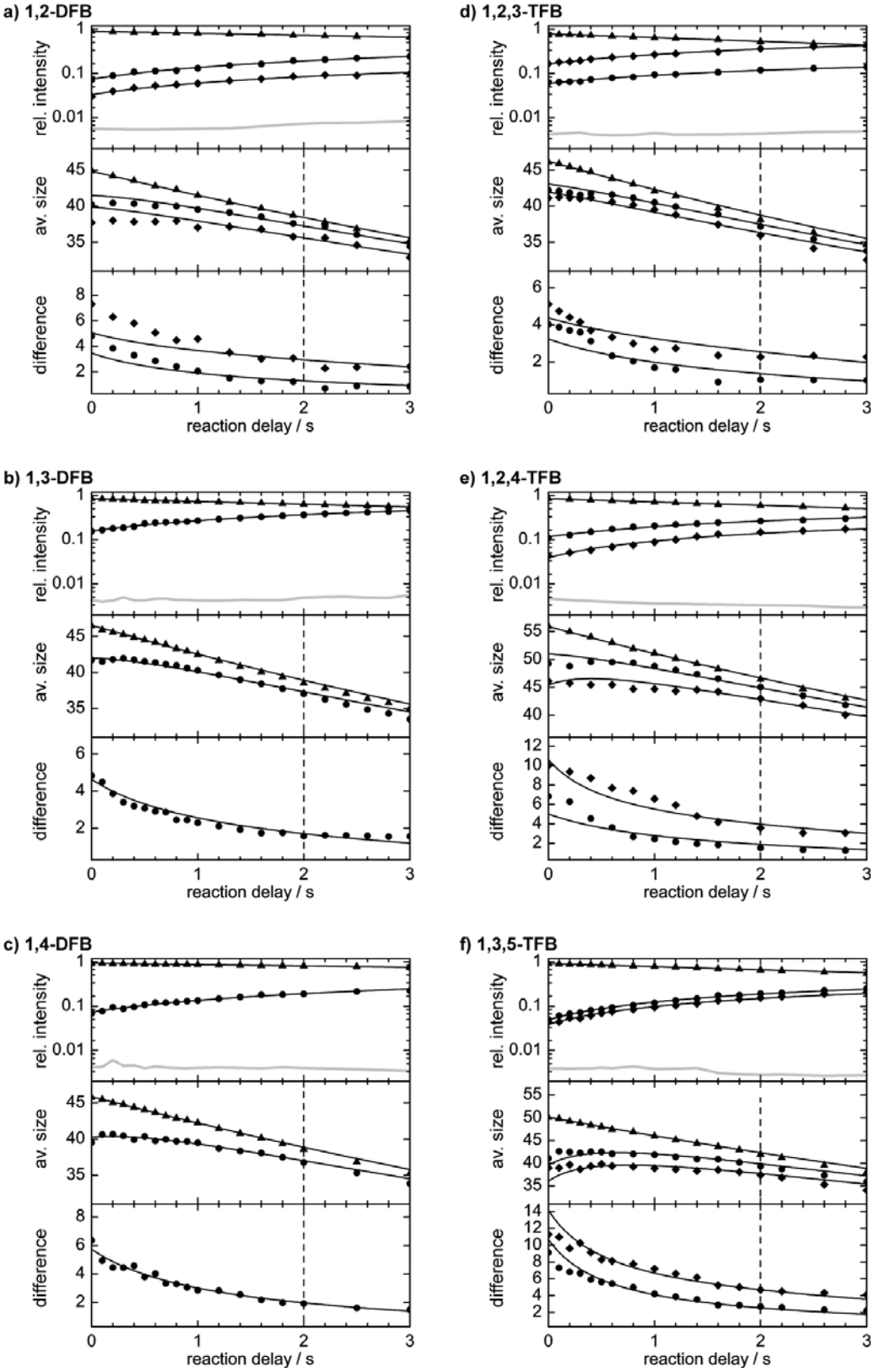

Figure S3

Kinetics and nanocalorimetric data analysis for all di- and trifluorobenzene isomers.

Table S1 Fit parameters for all reactions. $N_{0,R}$ and $N_{0,P}$ are the intercepts for the reactant and the product species, respectively, k_f is the slope, $N_R(t=0)$ and $N_P(t=0)$ are the initial cluster sizes and ΔN_{vap} the number of evaporated water molecules during the reaction.

Fit Parameter	k_f	$N_{0,e}$	$N_{0,OH}$	$N_{0,F}$	ΔN_{vap}(OH)	ΔN_{vap}(F)	$N_{el}(t=0)$	$N_{OH}(t=0)$	$N_f(t=0)$
		fixed	coupled	coupled	coupled	coupled			
1,2-$C_6H_4F_2$	0.0832	3.0000	5.3105	9.2479	0.6144	3.3589	44.8504	41.4840	39.8794
1,3-$C_6H_4F_2$	0.1000	3.0000	5.3105	—	0.6144	—	46.5525	42.0171	—
1,4-$C_6H_4F_2$	0.0895	3.0000	5.3105	—	0.6144	—	45.8969	40.2679	—
1,2,3-$C_6H_3F_3$	0.0959	3.0000	5.3105	9.2479	0.6144	3.3589	55.8857	50.9749	45.3842
1,2,4-$C_6H_3F_3$	0.0949	3.0000	5.3105	9.2479	0.6144	3.3589	46.2258	43.0878	41.9518
1,3,5-$C_6H_3F_3$	0.0911	3.0000	5.3105	9.2479	0.6144	3.3589	50.1289	39.5307	36.0448