Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Kinetics and mechanisms of polycondensation reactions between aryl halides and bisphenol A

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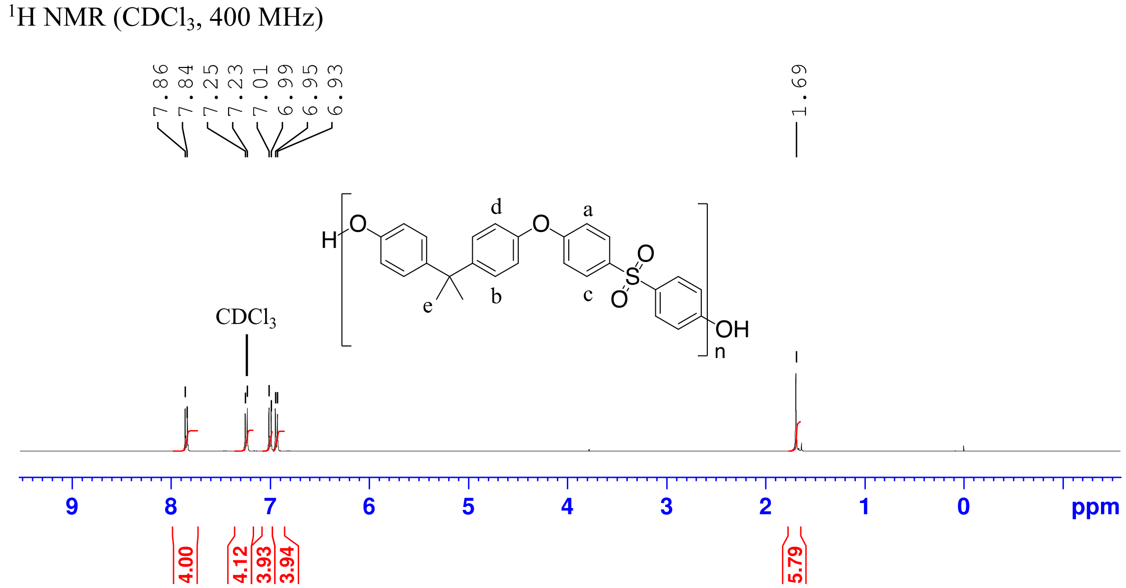

Figure S1. ^{1}H-NMR spectra (CDCl$_3$, 400 MHz) of a representative poly(arylene ether sulfone).

The following details the technique used to determine the kinetics (reaction conversion vs. reaction time) as well as the actual monomer concentrations. An example from the DFDPS/BPA reaction at 140 ˚C is provided. Aliquots were taken at 10 min, 15 min, 20 min, 30 min, 60 min, 120 min, 180 min, and 240 min from the beginning of the reaction, respectively. The number average molecular weight of the product from each aliquot was measured by SEC. The degree of polymerization was calculated from Mn by $X_n = M_n/M_0$, where M_0 is the molecular weight of the repeat unit of polysulfone as 442 g/mol. Then the conversion, p, was calculated as $p = 1-1/X_n$, when the stoichiometric ratio was assumed to be 1 after the hydrolysis side-reaction was compensated by the initial access amount of halide monomers. In terms of monomer concentration, the initial monomer concentration was set as 9.47 mmol/30.5 mL of solvents; the amount of monomer when each aliquot was taken for SEC was calculated as $n[M] = 9.47 * (1-p)$, and the total volume of the solvent at the moment V was taken as the difference between the initial volume of the solvents (V_0 = 30.5 ml) and the distilled solvents/water mixtures collected in the trap (V_d), as well as the amount of the aliquot taken each time (V_a), that is, $V = V_0 - V_d - V_a$; thus, the concentration of the monomer over the course of the reaction was calculated as [M] = n[M]/V from the values given above.

All relevant SEC traces for DFDPS polymerizations are shown in Figure S2, for DCDPS polymerizations are shown in Figure S3.

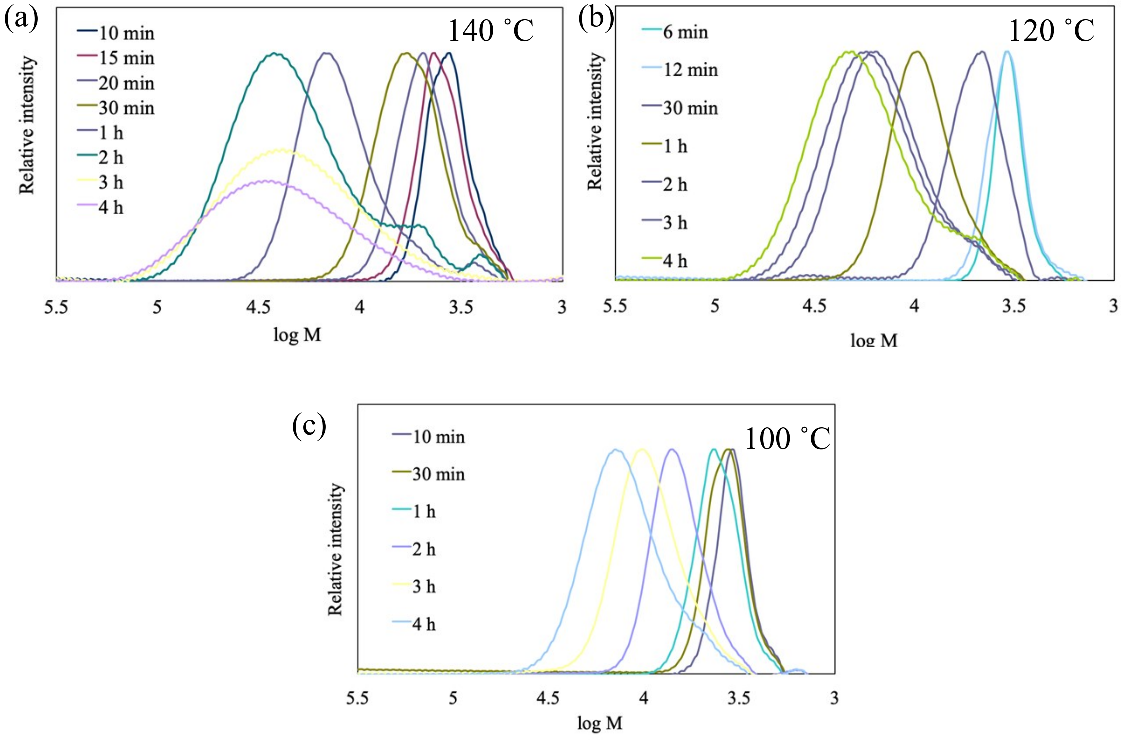

Figure S2. Size exclusion chromatography traces of poly(arylene ether sulfone)s from DFDPS/BPA polycondensation reactions with potassium carbonate performed at (a) 140 ˚C, (b) 120 ˚C, and (c) 100 ˚C as a function of time.

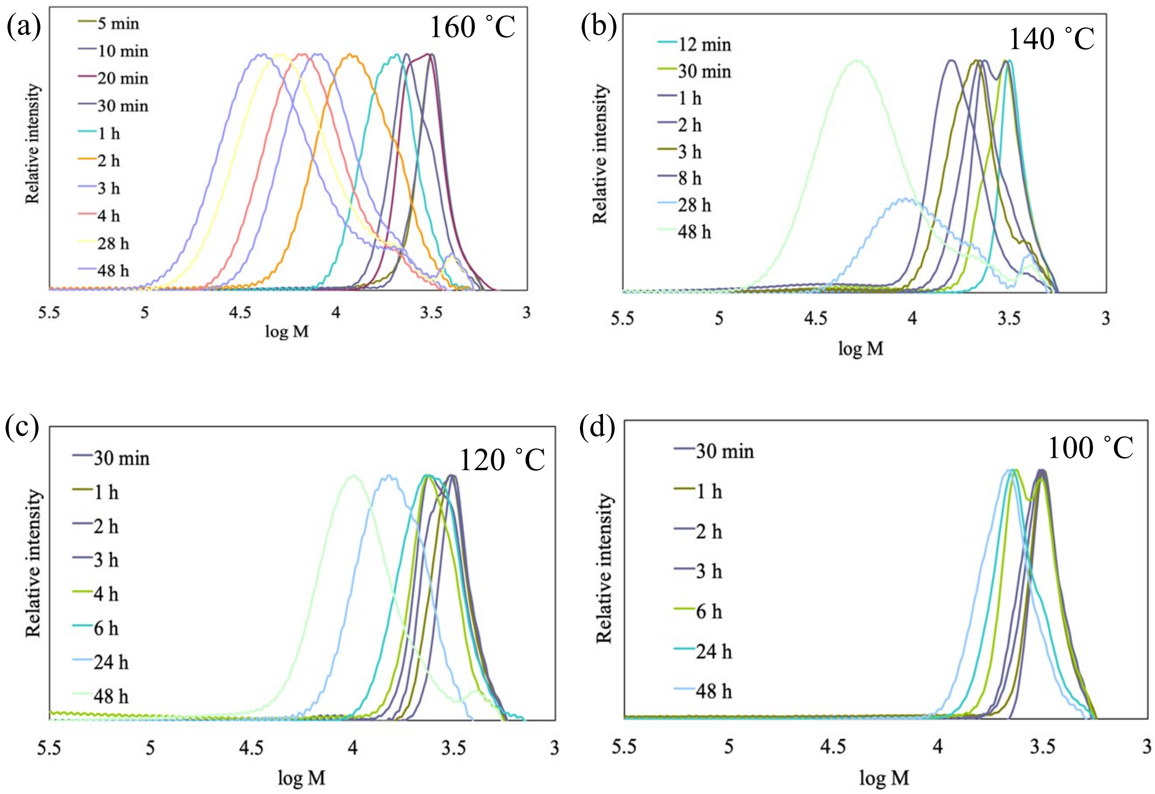

Figure S3. Size exclusion chromatography traces of poly(arylene ether sulfone)s from the DCDPS/BPA polycondensation reactions with potassium carbonate performed at (a) 160 ˚C, (b) 140 ˚C, (c) 120 ˚C, and (d) 100 ˚C as a function of time.

The evolution of Mn versus conversion for the DCDPS/BPA and DFDPS/BPA reactions are shown in Figure S4. These plots follow the classic plots predicted for step-growth polymerizations, wherein high conversion is needed to obtain a high molecular weight polymer.

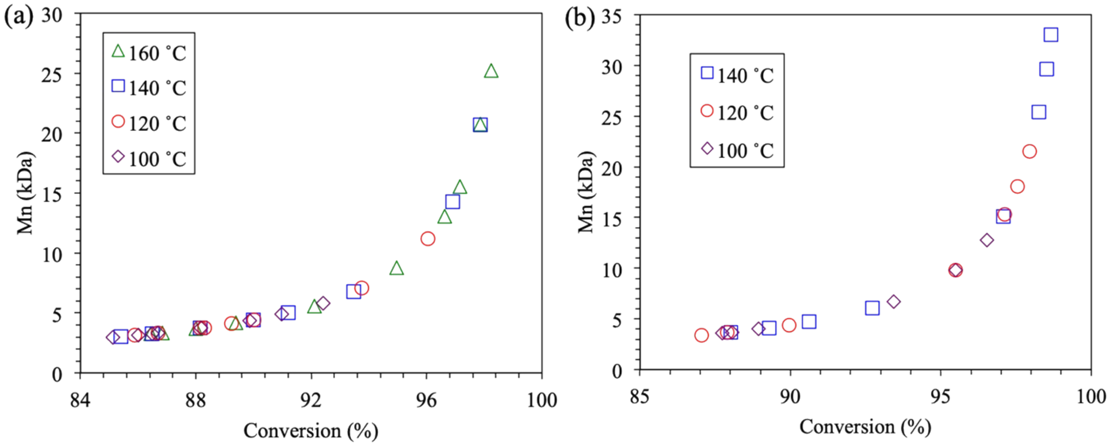

Figure S4. Number-averaged molecular weight (M_n) vs. reaction conversion for the polycondensation of: (a) DCDPS/BPA, and (b) DFDPS/BPA at various temperatures with K_2CO_3. Both plots for the DCDPS/BPA and DFDPS/BPA reactions showed typical step-growth polymerization behavior.

Polycondensation reactions with sodium carbonate as the base were performed for both DCDPS/BPA and DFDPS/BPA (Figure S5-6). The reaction rate of the polymerization with sodium carbonate is relatively lower than reactions that used potassium carbonate under identical experimental conditions. Importantly, the DFDPS/BPA reaction followed the same 2.5-order rate expression at lower conversions and a third-order rate expression at higher conversion. Similarly, a good fit to a second-order rate law for the DCDPS/BPA reaction was observed with sodium carbonate. Thus, it is confirmed that the change of the alkali metal in the base, in this case, is still compatible with the proposed mechanisms.

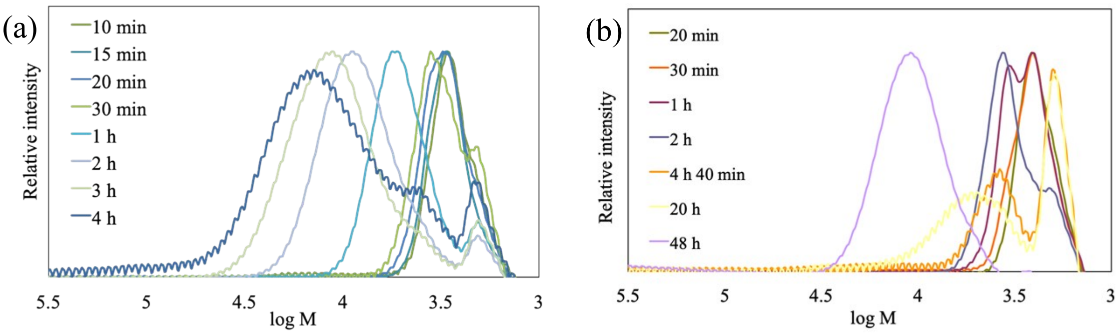

Figure S5. Size exclusion chromatography traces of poly(arylene ether sulfone)s from (a) the DFDPS/BPA polycondensation with sodium carbonate as a function of time at 140 ˚C, and (b) the DCDPS/BPA polycondensation with sodium carbonate as a function of time at 160 ˚C.

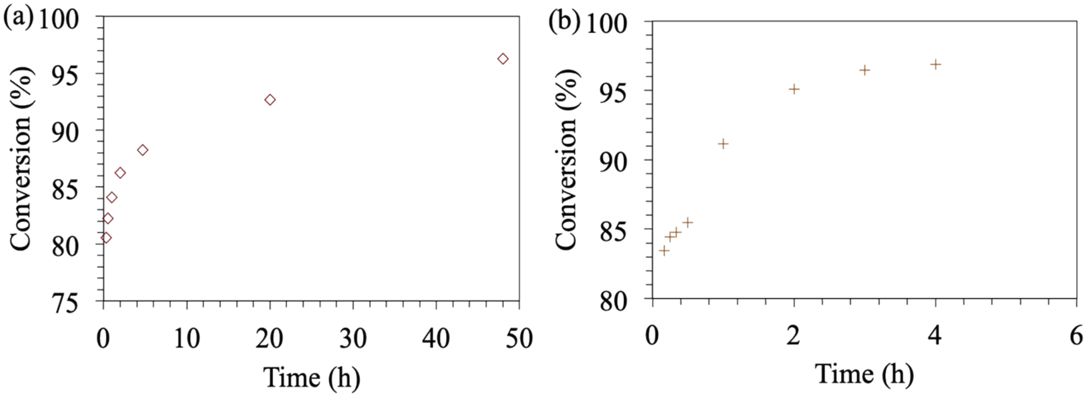

Figure S6. Conversion vs. reaction time plots for the polycondensation of: (a) DCDPS/BPA with sodium carbonate as the base at 160 ˚C, and (b) DFDPS/BPA with sodium carbonate as the base at 140 ˚C.

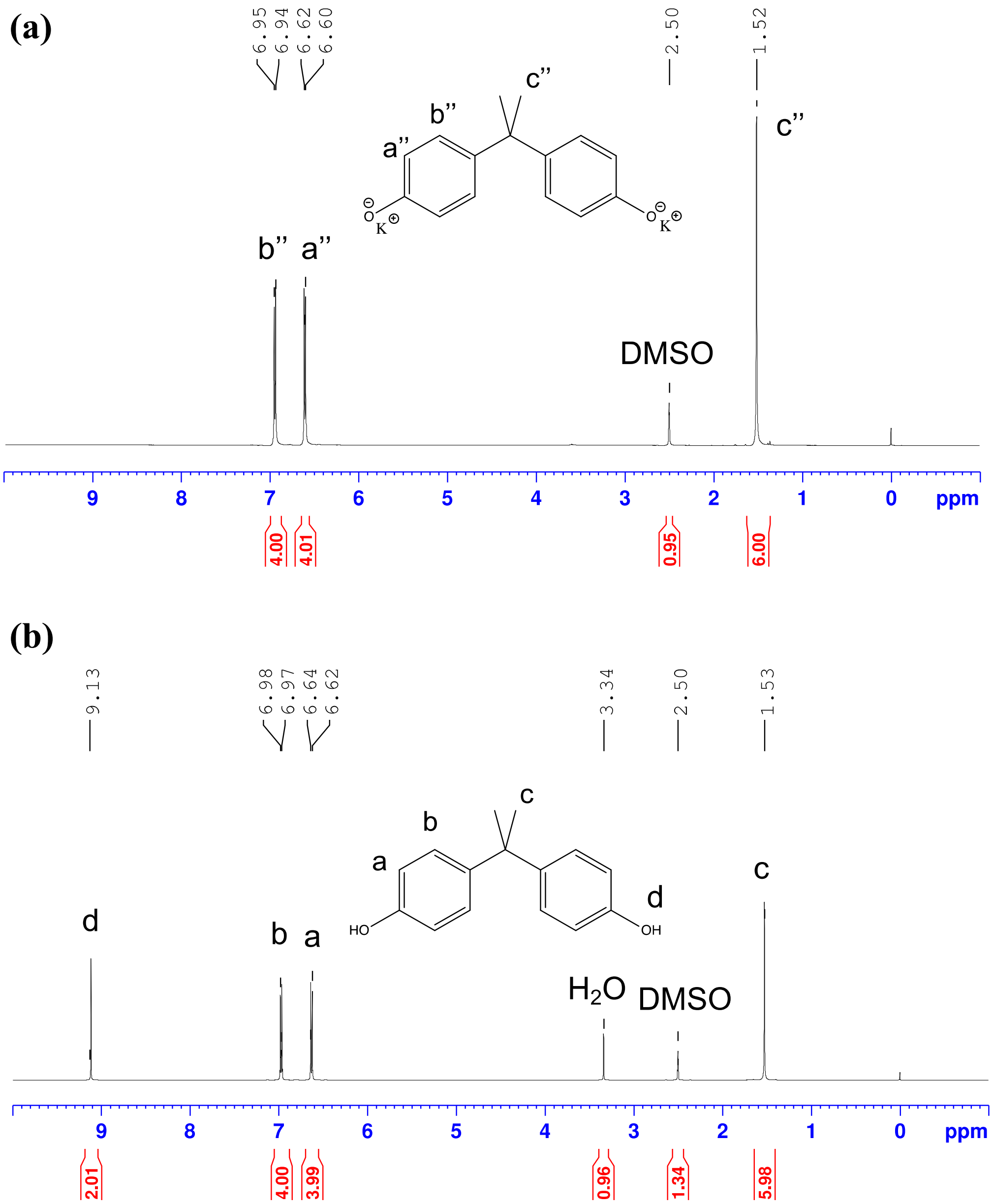

Figure S7. ^{1}H-NMR spectra (DMSO-d_6, 400 MHz) of (a) potassium phenolate and (b) bisphenol A.

In order to experimentally verify the interaction between the aryl fluoride and the potassium ion(s) from species B, potassium phenolate salt was first synthesized. To examine the synthesized potassium phenolate precursor’s chemical structure in ^{1}H NMR spectroscopy, deuterated dimethyl sulfoxide (DMSO-d_6) was used as the solvent for both the synthesized K^+PhO^- and bisphenol A. Samples contained 20 mg of dried monomer/precursor dissolved in DMSO-d_6. The chemical shifts are given in ppm downfield from tetramethylsilane (TMS), as shown in Figure S7. ^{1}H NMR spectrum of potassium phenolate (Figure S7a) (DMSO-d_6 with 0.05% v/v TMS, 400 MHz): $\delta = 6.94$ (4Hb", m, J = 9 Hz), 6.61 (4Ha", m, J = 9 Hz), 1.52 (6Hc", s). ^{1}H NMR spectrum of bisphenol A (Figure S7b) (DMSO-d_6 with 0.05% v/v TMS, 400 MHz): $\delta = 9.13$ (1Hd, s), 6.98 (4Hb, m, J = 9 Hz), 6.63 (4Ha, m, J = 9 Hz), 1.53 (6Hc, s). Upon deprotonation of the phenol group by the potassium carbonate, the peak from the phenol group vanished. This was indicative of the successful reaction between bisphenol A and potassium carbonate, and suggested complete conversion of bisphenol A into potassium phenolate.

^{19}F NMR spectra for DFDPS/K^+PhO^- complexes at varying molar ratios were collected. The chemical shift of fluorine shifted upward for DFDPS/K^+PhO^- mixtures relative to DFDPS (Figure S8a) as the ratio of DFDPS:K^+PhO^- increased in the order of 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5 (Figure S8b~f). This can be rationalized by a combination of the effects from electron density changes and paramagnetic contributions,[1] which is the subject of future investigations.

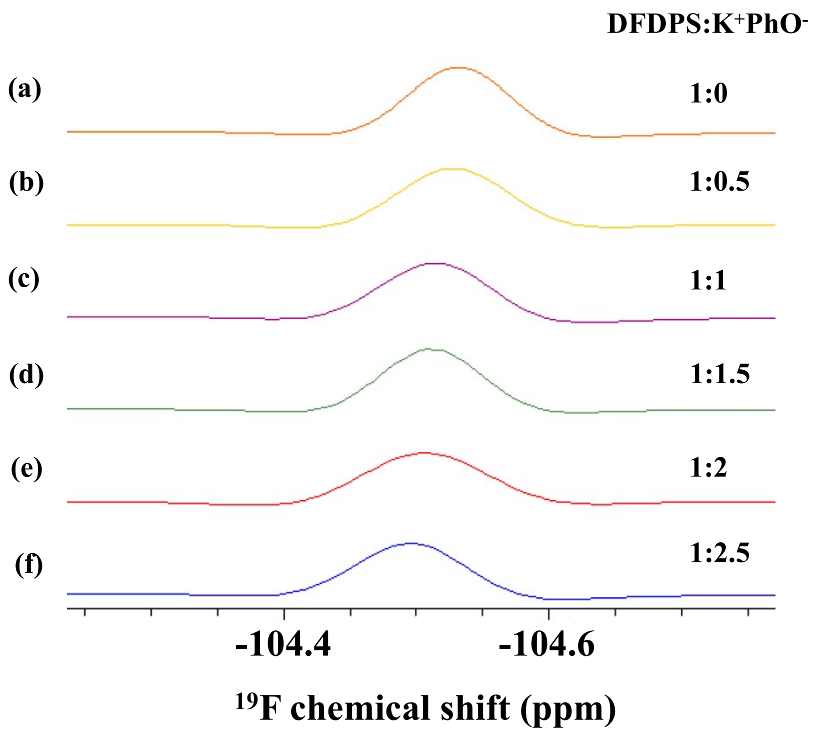

Figure S8. ^{19}F-NMR spectra (DMSO-d_6, 400 MHz) of DFDPS/K^+PhO^- homogenous mixture at room temperature with stoichiometric ratio of (a) 1:0, (b) 1:0.5, (c) 1:1.0, (d) 1:1.5, (e) 1:2.0, (f) 1:2.5, respectively.

Table S1. DFT calculations of the charge states and bond lengths of the related atoms upon complexation of DFDPS with Na^+PhO^- in various stoichiometric ratios.

<table>
<tr><td>F:Na^+ ratio</td><td>1:0</td><td>1:1</td><td colspan="2">1:2</td></tr>
<tr><td>F</td><td>-0.69 e^-</td><td>-0.70 e^-</td><td colspan="2">-0.71 e^-</td></tr>
<tr><td>Na^+-1</td><td>N/A</td><td>+0.92 e^-</td><td colspan="2">+0.93 e^-</td></tr>
<tr><td>Na^+-2</td><td>N/A</td><td>N/A</td><td colspan="2">+0.90e^-</td></tr>
<tr><td rowspan="2">F•••Na^+</td><td rowspan="2">N/A</td><td rowspan="2">2.26 Å</td><td>F•••Na^+-1</td><td>2.30 Å</td></tr>
<tr><td>F•••Na^+-2</td><td>2.69 Å</td></tr>
</table>

NOTE: Charges calculated in VASP using a 550 eV cut off energy at the GAMESS geometries, and the HSE06 functional

Additional comments related to Figure 5 in the main text: after the C-O and C-F bonds have formed and broken, respectively, the Na^+ cation of the NaX product is still complexed to the Ar-O-Ph molecule. It is uphill in energy by ~40 kJ/mol to break this complex for structures considered. If a second NaB is present, i.e. in the three-body case, a second de-coupling reaction must occur to from the final NaF (143 kJ/mol) or NaCl (125 kJ/mol) from NaX•••NaB (i.e., state 3 to 4 to 5 for the three-body mechanism and state 3 to 5 for the two-body mechanism). The strong complexation between NaX and NaB suggests that until NaX crystallizes and forms a solid, it acts to bind and thus trap NaB reactants.

1. References Cited

(1) Dahanayake, J. N.; Kasireddy, C.; Karnes, J. P.; Verma, R.; Steinert, R. M.; Hildebrandt, D.; Hull, O. A.; Ellis, J. M.; Mitchell-Koch, K. R. Progress in Our Understanding of 19F Chemical Shifts. In *Annual Reports on NMR Spectroscopy*; 2018. https://doi.org/10.1016/bs.arnmr.2017.08.002.