Supporting Information for

Kinetics study of heterogeneously continuous-flow nitration of trifluoromethoxybenzene

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Physical properties of TFMB and sulfuric acid solutions

Table S1 Physical properties of TFMB and sulfuric acid solutions

substance	Temperature K	μ *mPa·s*	ρ kg/m^3
TFMB	278	1.25	1226.3
	283	1.23	
	288	1.20	
	293	1.17	
Sulfuric acid (84 wt %)	278	35.1	1787.6
	283	28.9	1782.0
	288	24.5	1776.4
	293	20.5	1770.9
Sulfuric acid (82 wt %)	278	32.9	1769
	283	27.9	1762.9
	288	23.3	1758.6
	293	19.1	1753.2
Sulfuric acid (80 wt %)	278	29.6	1739.9
	283	25.3	1734.6
	288	21.7	1729.3
	293	18.3	1724.2
Sulfuric acid (75 wt %)	278	24.6	1687.3
	283	20.2	1682.4
	288	17.1	1677.4
	293	14.7	1672.6

TFMB: molecular weight=162.11 g/mol, boiling point=375 K.

Sulfuric acid: molecular weight=98.1 g/mol, boiling point=613 K.

Schematic diagram of setup for flow pattern observational experiment

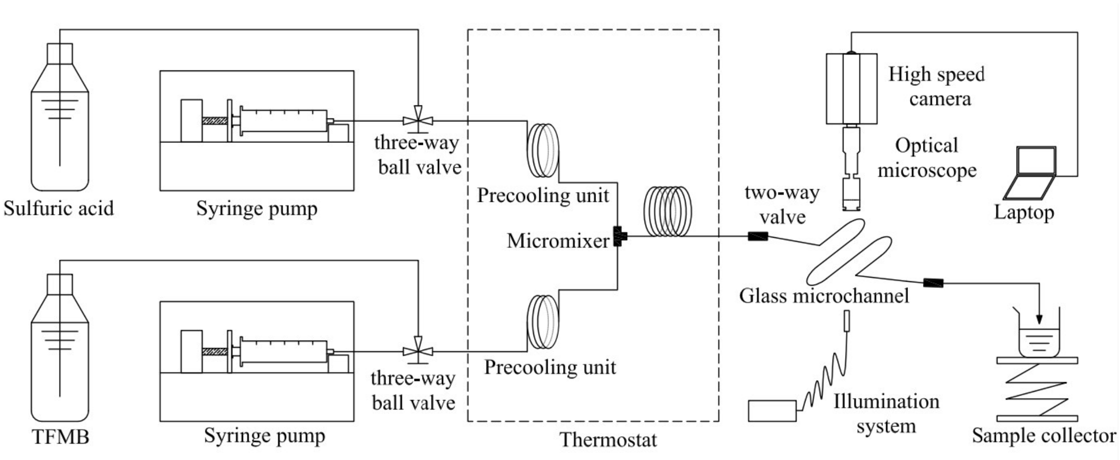


Figure S1 Schematic diagram of experimental setup for the flow pattern observation.

GC spectrogram of compounds involved in reaction

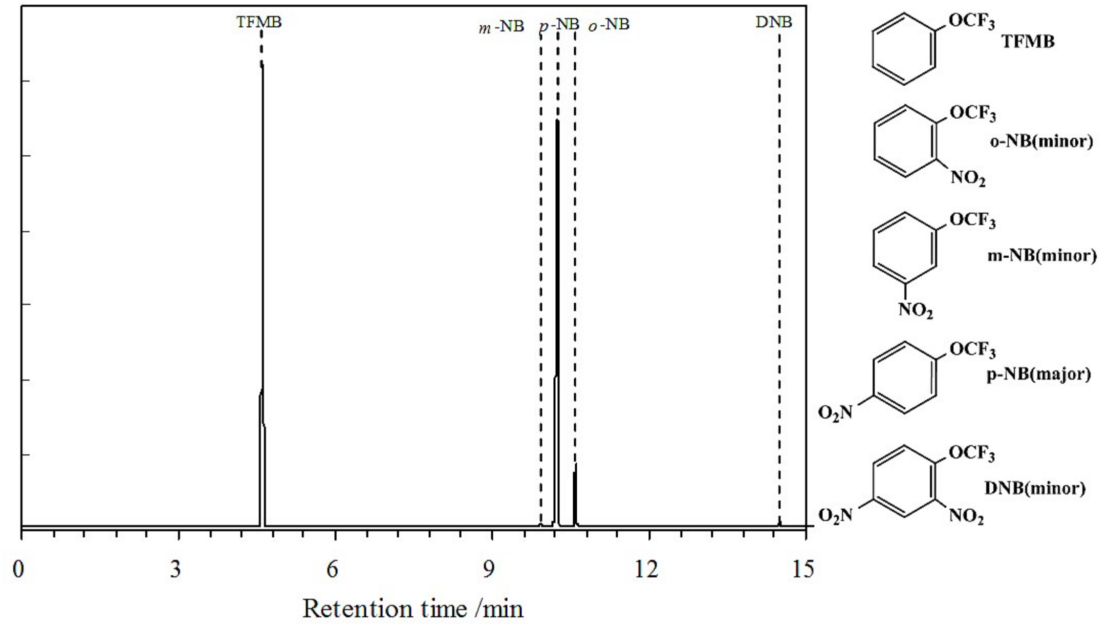


Figure S2 GC spectrogram of all compounds involved in the reaction.

Mass spectrum of p-(trifluoromethoxy) benzene sulfonic acid

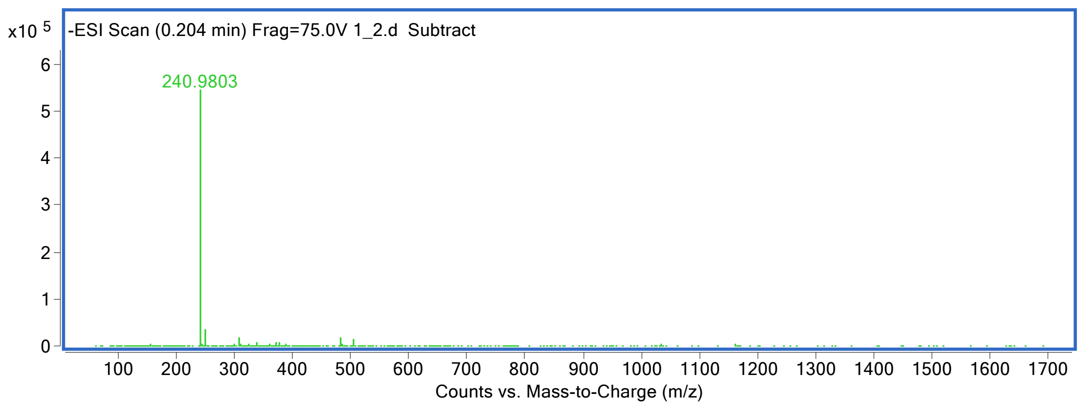


Figure S3 Mass spectrum of p-(trifluoromethoxy) benzene sulfonic acid.

Comparison of observed second-order rate constant

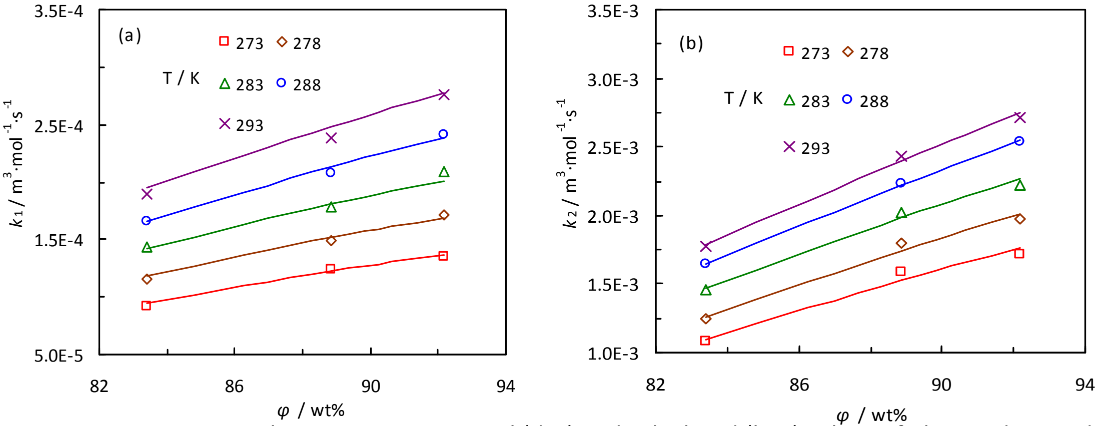
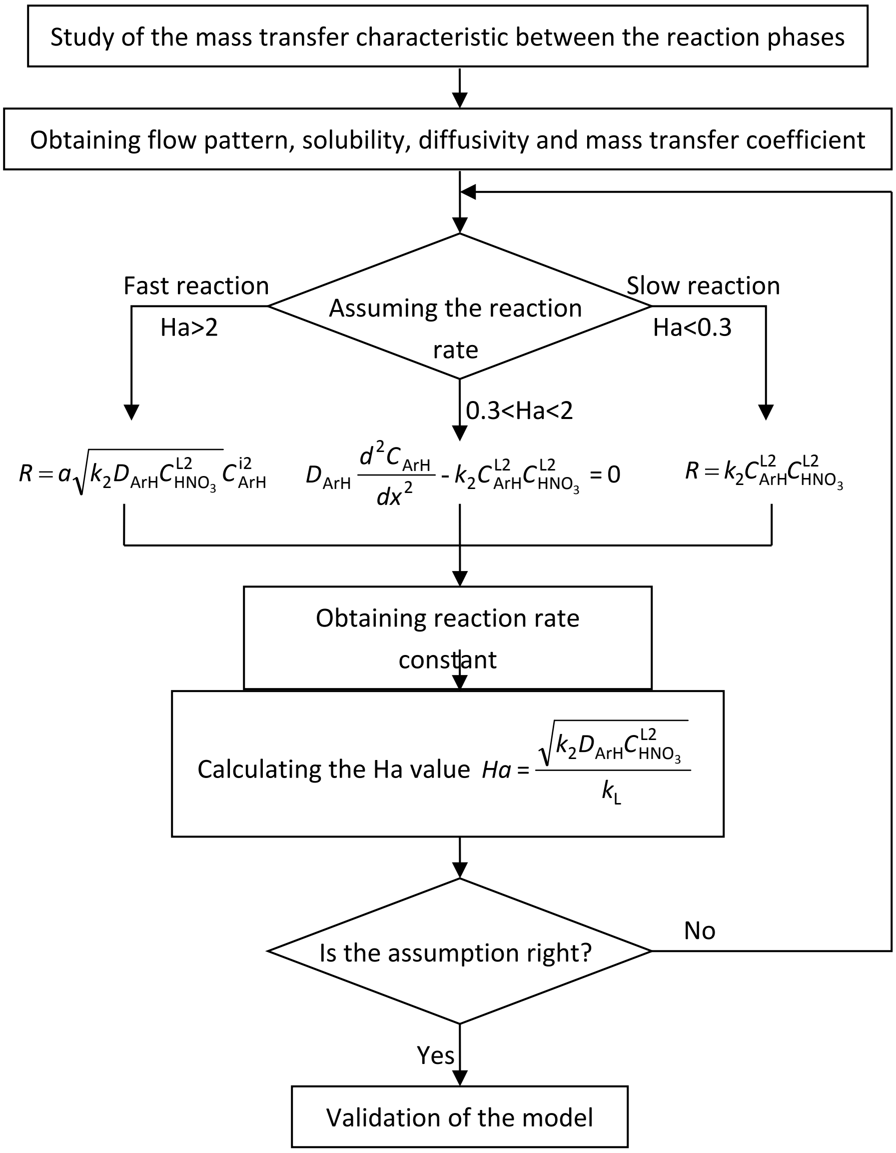


Figure S4 Comparison between experimental (dot) and calculated (line) values of observed second-order rate constant at different sulfuric acid strengths and temperatures (a) *o*-NB (b) *p*-NB.

Flow chart of the kinetic study



MATLAB program used for solving Eq.6

```
function odes_fit
format long
clear all
clc

k0 = [0 0];                              % Parameter initial value
lb = [0 0];                              % Parameter lower limit
ub = [+inf +inf];                        % Parameter upper limit

%Experimental data
%    t          B               pNB             oNB
data=...
    [ 0          0               0               0
      5.03      0.110439016     0.100248547         0.009951361
      7.54      0.155662656     0.141088625     0.014227765
      10.06     0.195082447     0.177579731     0.017108608
      12.57     0.251992372     0.227500878     0.023543548
      15.09     0.280506122     0.253835865     0.02528611
];
x0=data(1,2:end);
tspan = [data(:,1)'];
yexp = [data(2:end,2) data(2:end,3) data(2:end,4)];

% Using the function lsqnonlin()to estimate the parameters
[k,resnorm,residual,exitflag,output,lambda,jacobian] = ...
    lsqnonlin(@ObjFunc,k0,lb,ub,[],tspan,x0,yexp);
ci = nlparci(k,residual,jacobian);
fprintf('\n\nUsing the function lsqnonlint() to estimate the parameter values as follows:\n')
fprintf('\tk1 = %.9f \n',k(1))
fprintf('\tk2 = %.9f \n',k(2))

figure(1)

ts=0:((max(tspan)-min(tspan))/100):max(tspan);
[ts ys] = ode45(@KineticsEqs,ts,x0,[],k);
yy = [data(:,2) data(:,3) data(:,4)];
figure(1)
plot(ts,ys(:,1),'b',tspan,yy(:,1),'bo');
figure(2)
plot(ts,ys(:,2),'r',tspan,yy(:,2),'ro');
figure(3)
plot(ts,ys(:,3),'g',tspan,yy(:,3),'go');
figure(4)
```

```
plot(ts,ys(:,1),'b',tspan,yy(:,1),'bo',ts,ys(:,2),'r',tspan,yy(:,2),'ro',ts,ys(:,3),'k',tspan,yy(:,3),'ko')
legend('Calculated value of C1','Experimental value of C1','Calculated value of C2','Experimental value of C2','Calculated value of C3','Experimental value of C3','Location','best');

function f = ObjFunc(k,tspan,x0,yexp)                    % Objective function
[t Xsim] = ode45(@KineticsEqs,tspan,x0,[],k);
Xsim1=Xsim(:,1);
Xsim2=Xsim(:,2);
Xsim3=Xsim(:,3);

ysim(:,1) = Xsim1(2:end);
ysim(:,2) = Xsim2(2:end);
ysim(:,3) = Xsim3(2:end);

f = [(ysim(:,1)-yexp(:,1)) (ysim(:,2)-yexp(:,2)) (ysim(:,3)-yexp(:,3))];

function dCdt = KineticsEqs(t,C,k)                 % ODE model equation
C1=C(1);C2=C(2);C3=C(3);
k1=k(1);k2=k(2);
C0=8.4096;                                     % Saturate concentration of TFMB in sulfuric acid, mol/m3
M=0.8987;                                      % Ratio of initial molar of TFMB and nitric acid
dC1dt = (k(1)+k(2))*C0*(M-C(1));
dC2dt = k(1)*C0*(M-C(1));
dC3dt = k(2)*C0*(M-C(1));

dCdt = [dC1dt;dC2dt;dC3dt];
```