Dynamics of Cl + Propane, Butanes Revisited: A Crossed-Beam Slice Imaging Study

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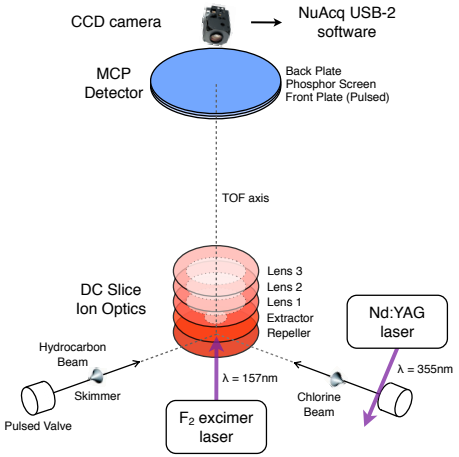
By taking advantage of an improved atomic chlorine source, we have measured velocity–contour flux maps of H–D abstractions in the reactions of chlorine with selected alkanes at an unprecedented level of detail. Angular and reduced translational energy distributions for the set of studied alkanes, namely propane, its two selectively labeled isotopologues $CD_3CH_2CD_3$ and $CH_3CD_2CH_3$, and butane isomers n-butane and isobutane for which none or only interpolated differential cross sections were measured in the past, show distinct differences that allow us to revisit the "reaction picture" of this family of reactions.

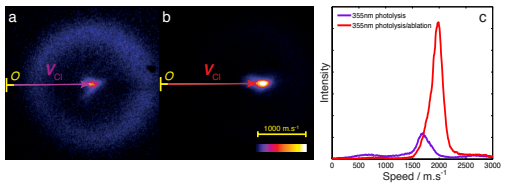
Experimental

Crossed-beam DC slice imaging set-up



- Radical hydrocarbon products are ionized with a VUB beam at 157nm.
- The ionized cloud is accelerated and stretched by a set of four ion optics lenses, and detected by a MCP/phosphor screen.
- Raw images are recorded using a CCD camera and our new acquisition program NuAcq-2.

A high-density Cl source: photolysis/ablation



- Raw images at m/z = 35 without (a) and with (b) ablation.
- Signal intensity multiplied by 4 in image a.
- (c) Corresponding chlorine beam profiles.

Advantages:
- Enhanced S/N ratio => Unfocused probe
  - Probe/interaction region overlap
  - Little density-to-flux correction
  - No multiple photon ionization
  => **Product selection with ionization energies**

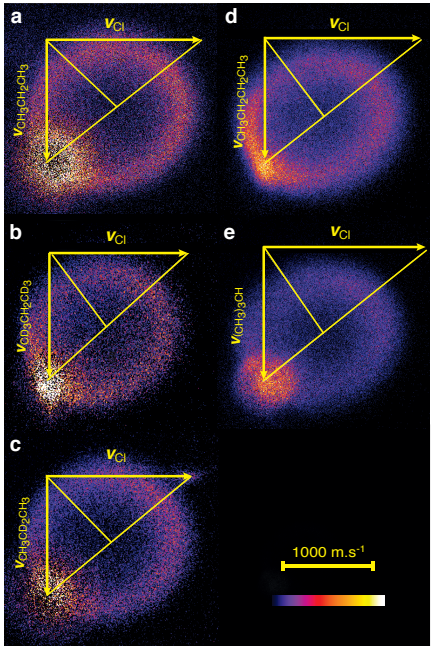
Thermochemical data

Reactant	Product	BDE (kcal mol^{-1})	$\Delta H(0\ K)$ (kcal mol^{-1})	Vertical IE (eV)	Adiabatic IE (eV)
Propane D1, D2	*n*-Propyl				
	$CH_2CH_2CH_3$	100.6	−2.8	8.40	7.66
	$CD_2CH_2CD_3$	103.1	−1.5	8.41	7.61
	$CH_2CD_2CH_3$	100.6	−2.8	8.42	7.64
	Isopropyl				
	CH_3CHCH_3	97.0	−6.4	7.74	7.47
	CD_3CHCD_3	97.3	−6.1	7.75	7.48
	CH_3CDCH_3	99.4	−5.2	7.73	7.46
n-Butane	*n*-Butyl				
	$CH_3CH_2CH_2CH_2$	100.5	−3.0	8.32	7.51
	2-Butyl				
	$CH_3CH_2CHCH_3$	97.3	−6.1	7.67	7.32
Isobutane	2-Methylene-propane				
	$(CH_3)_2CHCH_2$	100.6	−2.8	8.33	6.64
	Isobutyl				
	$(CH_3)_3C$	95.3	−8.1	7.22	6.87

- Bond dissociation energies (BDEs) and reaction enthalpies at 0 K (DH(0 K)) for all the possible H–D abstractions, and adiabatic and vertical energies of the corresponding products.
- Values calculated at the CBS-QB3 level of theory.

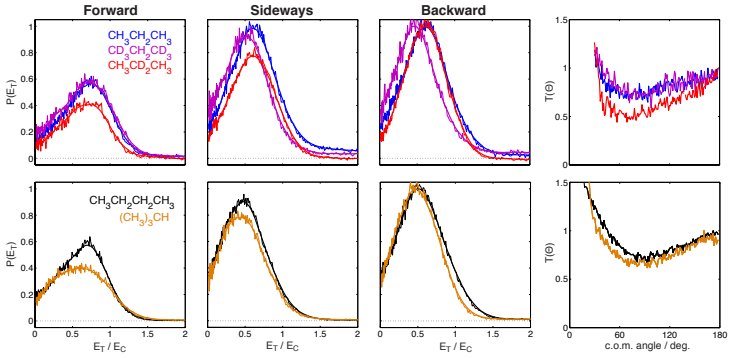
=> **Velocity–flux maps measured for secondary H(D) abstractions in propane and n-butane, and tertiary H abstraction in isobutane.**

Imaging

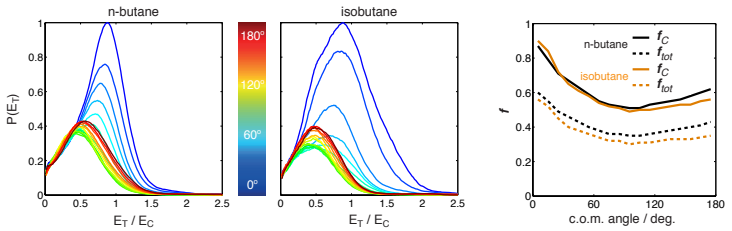


DC sliced raw images of reactive scattering and nominal Newton diagrams for the reactions of chlorine with propane and butane: (a) propane, E_C = 11.6 kcal.mol^{-1} (b) propane D1, probe at m/z = 49 (CD3CHCD3) E_C = 11.8 kcal.mol^{-1}, (c) propane D2, probe at m/z = 46, (CH3CDCH3) E_C = 12.1 kcal.mol^{-1}, (d) n-butane, probe at m/z = 57, E_C = 13.4 kcal.mol^{-1}, and (e) isobutane, probe at m/z = 57, E_C = 13.6 kcal.mol^{-1}. All images are shown after background subtraction and density-to-flux correction.

Differential Cross Sections



- Reduced translational energy distributions for forward (30–60 deg.), sideways (60–120 deg.), and backward (120–180 deg.) scattered products and the center-of-mass angular distributions.
- Top panel corresponds to propane reactions. Bottom panel corresponds to butane reactions.
- Each distribution is normalized to its backward component that dominates the translational energy distributions of all the systems in this range of integrated angles.



- Left: Reduced translational energy distributions for 10 deg. steps of the angular distributions of reactions of chlorine with n-butane and isobutane.
- Right: Fractions f_C and f_{tot} of collision energy E_C and available energy E_{tot}, respectively.

Conclusions

Propane and isotopologues:
- Concerning translational energy recoil, FW and SW $CD_3CH_2CD_3$ distributions peak at lower ET* than regular propane and $CH_3CD_2CH_3$, while all FW distributions peak at similar ET*, reflecting a more effective energy disposal into the CD3CHCD3 propyl degrees of freedom for the "rebound-like" mechanism.
=> **the role of vibrational excitation of the propyl product**
- The angular distribution of D2 is affected by the deuteration.
=> **a kinematic effect**

Butane isomers:
Compared to n-butane distributions, isobutane distributions exhibit a more sharply peaked angular distribution with a broader translational energy distribution in the FW direction, even possibly a bimodal distribution.
=> **vibrationallly excited HCl or steric hindrance effect?**
=> Need for state-resolved experiments

This work is funded by
U.S. DEPARTMENT OF ENERGY