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Vibrationally resolved dynamics of the reaction of Cl atoms with 2,3-dimethylbut-2-ene in chlorinated solvents

Fawzi Abou-Chahine, Stuart J. Greaves,[‡] Greg T. Dunning and Andrew J. Orr-Ewing*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Gregory M. Greetham, Ian P. Clark and Michael Towrie

Central Laser Facility, Research Complex at Harwell, Science and Technology Facilities Council,
Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11
0QX, UK

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[‡] Current address: Department of Chemistry, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK.

1. Constraints imposed on the kinetic model

The kinetic model of equations (5a-i) of the main paper contains 7 rate coefficients and the fits require further determination of the ratio of squares of the transition dipole moments for the (2-1) and (1-0) infra-red bands of HCl (μ_{21} and μ_{10} respectively), and the asymptotic yield of HCl at long times. Numerical integration of the kinetic model to fit data sets such as those displayed in figure 5 was therefore over-parameterized and constraints were imposed on some of the parameters. The choice of constraints was made using careful analysis of the correlations between parameters and uncertainties in the derived values to produce a robust fitting method, and the following list summarizes our procedures.

(i) The ratio of the squares of the transition dipole moments, $(\mu_{21}/\mu_{10})^2$, was fixed at a value of 2.0, motivated by the outcomes of trial fits that returned preferred values in the range 2.0 – 2.5 and by the results from IR-pump and IR-probe data discussed in section A of the main paper. This value is as expected for a harmonic oscillator.¹

(ii) The rate coefficients k_{rc} for HCl vibrational relaxation in-cage were set to be zero, because trial fits returned values much lower than the rate coefficients for diffusion into the bulk solvent. The majority of vibrational relaxation is therefore expected to occur in the bulk via pathway (5i).

(iii) The value of k_{rb} was constrained using information from the IR pump and probe experiments described in section A of the main paper. In those experiments, the HCl vibrational relaxation time constant of 50 ps in the presence of ~ 1 M DMB corresponds to a pseudo-first order rate coefficient of 0.02 ps^{-1} . In the absence of DMB the relaxation rate is two orders of magnitude slower. We therefore constrained k_{rb} to respective values of 0.005, 0.01 and 0.015 ps^{-1} for measurements using 0.25, 0.5 and 0.75 M solutions of DMB, regardless of whether they were conducted in CCl_4 or CDCl_3 because the dominant HCl($v=1$) relaxation pathway appears to be near-resonant coupling to the DMB.

(iv) Amplitudes of the signals were not floated as free parameters, but were instead constrained by requiring them to converge to the asymptotic HCl (1-0) band absorption intensities (taken to be the values observed at 1000 ps). The *relative* amplitudes of the HCl (2-1) band data therefore depended on the relative populations of HCl($v=1$) and HCl($v=0$) at any given time and the transition dipole moment ratio $(\mu_{21}/\mu_{10})^2$, and were a determining factor of the fit outcomes.

(v) Fits were performed simultaneously to HCl(1-0) and HCl(2-1) band data sets for two different DMB concentrations. We then verified that the resultant parameters described well the time-

dependence of the data for a third concentration. For experiments in CDCl_3 this analysis proved most robust when simultaneously fitting data for 0.25 M and 0.5 M DMB, then checking that the fitted results simulated successfully the 0.75 M DMB data by adjusting only the total amplitude of the signals. For experiments in CCl_4 , simultaneous fits were performed to 0.5 M and 0.75 M DMB data, and the outcomes used to simulate the 0.25 M data. Simultaneous fits to all three concentrations were less satisfactory, most likely because in each case data for one particular concentration showed poorer signal to noise ratios because of slow drifts from the optimum alignment of the IR and UV laser beams.

2. Competitive adduct formation in the Cl + DMB reaction

Gas phase reactions of Cl atoms with alkenes exhibit competition between a direct H-atom abstraction pathway and an addition mechanism, forming adducts that might subsequently eliminate HCl if they are not collisionally stabilized.²⁻⁵ The kinetic analysis of data presented in the main paper, using reaction (5a-i) does not explicitly take adduct formation into account. We regard addition-elimination to be an unlikely source of HCl because of rapid collisional stabilization of the addition complex by solvent molecules, and a subsequent barrier to elimination that we calculate to be $\geq 30 \text{ kJ mol}^{-1}$. The direct abstraction mechanism is therefore expected to dominate HCl production. However, competition between two pathways for loss of Cl:



(with $\{\text{Cl-RH}\}$ denoting the adduct) may influence our analysis because (ESI_2) is an additional sink for Cl atoms, and the rate of formation of HCl will be controlled by the combined rate of both the above reactions. The procedure adopted in the main paper to calculate $\Gamma(v=1)$, the fractional branching into $\text{HCl}(v=1)$, uses values of rate coefficients derived from the kinetic fits to the model of equations (5a-i). However, this branching can also be estimated from the relative *amplitudes* of the $\text{HCl}(v=1)$ and $\text{HCl}(v=0)$ absorption signals, which will not be affected by competitive adduct formation. Here, this alternative analysis is summarized to demonstrate the robustness of our determination of $\Gamma(v=1)$. Time-dependent ratios of signal intensities obtained in absorption via the (2-1) and (1-0) vibrational bands of HCl were calculated from data of the type displayed in figure 5 of the main paper. After the first 5 ps, the ratios decay with time because of vibrational relaxation, and we therefore focus on the first 55 ps and linearly extrapolate to $t = 0$ ps to estimate unrelaxed ratios.

We denote the number of HCl molecules initially formed in $v=0$ by n_0 and the number formed in $v=1$ by n_1 , from which it follows that:

$$\Gamma(v = 1) = \frac{n_1}{n_0 + n_1} \quad (\text{ESI}_3)$$

The intensities of the (2-1) and (1-0) bands depend on the transition dipole moments and the populations of $v=0$ and 1, thus:

$$\frac{I_{21}}{I_{10}} = \frac{n_1 \mu_{21}^2}{(n_0 - n_1) \mu_{10}^2} = \frac{2n_1}{(n_0 - n_1)} \quad (\text{ESI}_4)$$

where the ratio of squares of transition dipole moments has been taken to be 2.0 (the harmonic oscillator ratio). This expression assumes no HCl is formed in $v=2$, which is expected to be energetically inaccessible, and is not observed experimentally. Rearrangement of these two expressions allows calculation of $\Gamma(v=1)$ for the reaction products from the ratio of intensities of the two HCl bands extrapolated to $t = 0$ ps. The outcomes are listed in **Table ESI_1** as averages of four measurements for each solvent.

Solvent	$\Gamma(v=1)$
CDCl_3	0.27 ± 0.02
CCl_4	0.18 ± 0.02

Table ESI_1: Values of the HCl($v=1$) branching fraction from reaction of Cl + DMB in solution in CDCl_3 and CCl_4 , estimated using the relative intensities of the observed HCl (2-1) and (1-0) IR bands. Values are the average of four measurements, with uncertainties reported as 1 SD.

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