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Reply [to "Comment on 'Indications of photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California' by D. D. Parrish et al."]

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Reply

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Chlorine atom chemistry in the marine boundary layer is a topic that has received considerable recent attention [see *Finlayson-Pitts*, this issue, and references therein]. In her comment, Finlayson-Pitts has pointed out that the observed slope of the *n*-butane to ethane versus propane to ethane correlation in Figure 9 of *Parrish et al.* [1992] is in closer agreement with Cl kinetics than the OH kinetics that was considered there and that this agreement may indicate that Cl atoms make a substantial contribution to the removal of the light alkanes from the tropical and temperate marine troposphere. However, we believe that much more substantial evidence must be presented for this conjecture before it can be accepted. Moreover, evidence presented below suggests that Cl atom chemistry is unlikely to play a significant role, at least in the removal of light alkanes from either the continental or the marine troposphere in tropical and temperate regions.

As discussed semiquantitatively in the appendix of *Parrish et al.* [1992] and earlier by *McKeen et al.* [1990], the mixing of air masses of different ages leads to a systematic deviation from the slope expected from the kinetics of the removal processes. Recently, S. A. McKeen and S. C. Liu (Hydrocarbon ratios and photochemical history of air masses, submitted to Geophysical Research Letters, 1993) have quantitatively reproduced the observed slope from a three-dimensional model of the chemistry and mixing in the troposphere over the western Pacific region. This model included only OH removal of the alkanes. If the effects of mixing are not treated adequately, the slopes of plots such as Figures 9 and 10 of *Parrish et al.* [1992] cannot be utilized to distinguish between the roles of different removal processes. Nevertheless, two arguments lead us to conclude that Cl atom chemistry plays no more than a minor role in the removal of the light alkanes from the tropical or temperate marine boundary layer. First, Figure 10 of *Parrish et al.* [1992] includes continental and free troposphere data as well as marine data. All of these data are reasonably well fit (r^2 = 0.89) by a straight line with a slope (1.47) similar to that found in the Point Arena data alone (1.33) and in the North Atlantic (1.66) by *Rudolph and Johnen* [1990]. Recently, *Jobson et al.* [1993] have presented a similar plot for data collected at

Fraserdale, Ontario (latitude 50° N, longitude 82° W), a remote boreal site in eastern central Canada; for this continental data set they found a slope of 1.44 with an r^2 of 0.96. All of these slopes are in remarkable agreement, and all are significantly smaller than predicted by OH kinetics, which is 2.75 ± 0.55 (confidence limit calculated from 2σ confidence limits of rate constants (R. Talukdar and A. R. Ravishankara, private communication, 1993) and a 250 to 298 K temperature range). These relatively small slopes are characteristic of the free troposphere and continental air masses as well as the marine boundary layer. Yet, the marine boundary layer is the only region of the troposphere where the Cl atom sources cited by Finlayson-Pitts [this issue] could conceivably lead to a substantial contribution to alkane removal.

Second, there are correlation plots of alkane concentration ratios that can give more direct information regarding the relative contributions of Cl atom and OH radical reactions to alkane removal, regardless of the effects of mixing. Table 1 gives kinetic data for the reactions of C_2-C_4 alkanes with Cl and OH. The values of the relevant rate constants are such that the Cl reactions will change the ratio of the two isomers of butane but will leave the *i*-butane to propane ratio relatively constant. In contrast, OH reactions will leave the ratio of the butanes relatively constant but will change the *i*-butane to propane ratio. Thus a log-log plot of the ratio of *i*-butane to *n*-butane versus *i*-butane to propane should provide two approximately orthogonal axes that will separate the Cl and OH contributions to alkane removal. Furthermore, if one of these two ratios does indeed remain constant, then mixing of two air masses of different ages cannot affect that ratio since it would have the same value in both. Of course, this assumes that the source ratios are relatively constant; the data presented below suggest that this is indeed true.

Figure 1 compares experimental data with the behavior expected from the reaction kinetics under five scenarios with differing contributions from Cl and OH reactions. (The format chosen for the plot is log-log rather than a linear plot of the logs of the ratios as in Figures 9 and 10 of *Parrish et al.* [1992]. The alkane present in the lowest concentrations and therefore subject to the greatest experimental uncertainties is placed in the numerator, and the most precisely determined ratio is used as the abscissa. Only data with *i*-butane concentrations greater than twice the detection limit are included in the plot, although the full data sets were used in the linear, least squares fits discussed below.) The OH kinetics provide a mechanism for the evolution of the ratios characteristic of the urban emission source areas to the ratios observed in aged marine (Atlantic data) and continental (Boulder data) areas in Figure 1*b*. These

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TABLE 1. Radical Kinetic Data for Reactions With Alkanes

	Cl		OH	
	k (X 10¹¹)*	ΔE/R†	k (X 10¹³)‡	B‡
Ethane	6.38	90±90	2.14	-462±43
Propane	13.4	-40±250	10.0	-44±42
n-Butane	19.7	—	23.3	190±64
i-Butane	13.7	—	21.9	277±49

Units, cm³ s⁻¹ for k, K for ΔE/R, and for B.

*[Atkinson and Aschmann, 1985]. Data are for 296 K; the values are nearly independent of temperature.

†[DeMore et al., 1992].

‡[Atkinson, 1989]. Values calculated for 280 K; the temperature dependences (given by T²eᴮ/ᵀ) partially cancel so that the derived slopes are only weakly temperature dependent.

data are in excellent agreement with the Point Arena data of Figure 1a. In contrast, the Cl kinetics would tend to move the ratios perpendicular to the trend of the data and cannot account for the evolution of the ratios from source to remote regions.

Table 2 compares the slopes derived from weighted, linear least squares fits of the log-transformed data with the slopes expected from the reaction kinetics. The fitting routine allowed for uncertainties in both ratios and weighted each datum with the inverse square of its 1σ confidence limit. This confidence limit was propagated from the confidence limits of the measured hydrocarbon concentrations used to calculate the ratio. The confidence limit of each hydrocarbon measurement was set equal to the greater of either the quoted precision of the

measurement or the ratio of the quoted detection limit to the measured concentration. The 2σ confidence limit of the slope derived from this weighted least squares fit is also given in Table 2. All of the experimental slopes are consistent with OH kinetics alone; there is no evidence to support the hypothesis that Cl kinetics must make a significant contribution. This conclusion is consistent with the observed constancy of the i-butane to n-butane ratio in marine [Rudolph and Johnen, 1990; Hov et al., 1991] and continental [Jobson et al., 1993] data sets.

Pszenny et al. [1993] have presented simulations for four scenarios of photochemistry in the marine boundary layer, including both Cl atoms and OH radicals. They assumed unidentified "missing" sources of Cl_2 or HOCl of 570, 290, and 50 parts per trillion by volume (pptv) Cl per hour in scenarios B, C, and D, respectively, which resulted in corresponding Cl atom concentrations of 2.6 X 10⁵, 1.4 X 10⁵ and 1.4 X 10⁴ cm⁻³. The slope calculated for each of these three simulations lies outside the 2σ confidence limits of the observed slopes from all three data sets, including the two from marine surface sites; the data simply do not exhibit the relatively large negative slope that would indicate a substantial Cl atom contribution. However, given the uncertainties in the experimentally derived and kinetically expected slopes and the uncertainty of the effects of mixing upon the slopes, chlorine atom contributions of the magnitude of simulation D perhaps cannot be rigorously excluded. Cl atom concentrations of approximately 10³ cm⁻³ as predicted by Singh and Kasting [1988] and scenario A [Pszenny et al., 1993] are certainly compatible with the data.
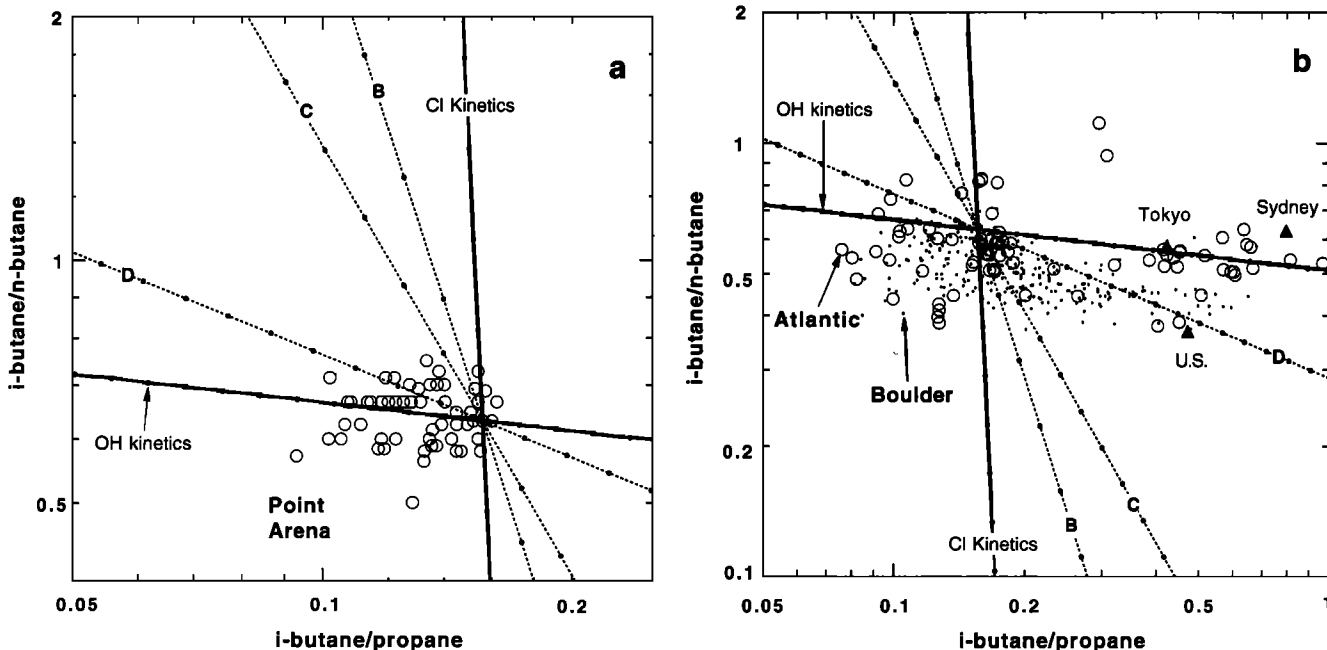

Fig. 1. Log-log plots of two alkane concentration ratios. The data are from (a) spring 1985 at Point Arena [Singh et al., 1988], the same data set considered by Parrish et al. [1992], and (b) spring 1987 at the surface of the Atlantic Ocean [Rudolph and Johnen, 1990] and winter 1991 at Boulder, Colorado (P. D. Goldan and W. C. Kuster, unpublished data, 1991). The three triangles in (b) give the ratios from the urban data sets in Table 1 of Parrish et al. [1992]. The nearly horizontal and vertical solid lines show the behavior expected for solely OH and Cl removal reactions, respectively. The dashed lines were calculated from the relative OH and Cl contributions from the indicated simulations of Pszenny et al. [1993]. All of these lines were calculated to pass through a point of the Point Arena data sets that is representative of the higher and least aged concentrations of the alkanes. The solid circles along the solid and dashed lines indicate the change expected in one day assuming diurnally averaged concentrations of OH = 1X10⁶ cm⁻³ and Cl = 5X10⁴ cm⁻³ for the solid lines and 25% of the Cl and OH number densities given for noon by the scenarios of Pszenny et al. [1993] for the dashed lines.

TABLE 2. Experimental and Theoretical Slopes for the Log-Log
Relationships of the i-Butane to n-Butane Ratio Versus
i-Butane to Propane Ratio Plots

Scenario	Slope	Confidence Limit, 2σ
Experimental Procedure		
Point Arena, California	+0.22	0.30
Atlantic Ocean	-0.077	0.05
Boulder, Colorado	-0.17	0.003
*Theoretical Procedure**		
OH kinetics only	-0.17	$-0.9 < $ slope $ < 0.4$†
Cl kinetics only	-20	lslopel > 6‡
Simulation B §	-3.18	
Simulation C §	-1.77	
Simulation D §	-0.43	

*From equation (7) of *Parrish et al.* [1992] and rate constants of Table 1.

†Calculated from the 2σ confidence limits of rate constants (R. Talukdar and A. R. Ravishankara, private communication, 1993) for a 250 to 298 K temperature range.

‡The absolute value of the slope is greater than 6, based on the 2σ confidence limits of *Atkinson and Aschmann* [1985].

§Based on the relative amounts of Cl and OH from *Pszenny et al.* [1993].

In summary, the Point Arena light alkane measurements, when examined in a format designed to distinguish between OH and Cl removal mechanisms, do not provide any evidence indicating a significant contribution from Cl atoms; OH kinetics alone are adequate to explain the data. This conclusion is also consistent with the Atlantic data set of *Rudolph and Johnen* [1990]. The deviations from the behavior expected strictly from OH kinetics noted by *Parrish et al.* [1992] must indeed be attributed to the mixing processes discussed therein.

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