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# Polar sunrise experiment 1995: hydrocarbon measurements and tropospheric Cl and Br-atoms chemistry

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## Abstract

As part of the Polar Sunrise Experiments (PSE) 1995, we report our results on measurement of non-methane hydrocarbons (NMHC) collected at Alert, Northwest Territories, Canada (82.5° N, 62.3° W) from Julian days 57 to 113, 1995 along with our data on continuous methane and ozone measurements during the same period. The concentration of NMHCs such as alkanes correlated well with that of methane during the dark period before polar sunrise. However, no correlation was observed after the sunrise. Several ozone depletion events and concurrent decreases in hydrocarbon concentrations relative to their background levels were observed. In all ozone depletion periods, concentration changes of alkanes and toluene were consistent with the occurrence of Cl-atom reactions. The characteristics of alkane isomer concentration changes suggest the dominance of HO chemistry prior to, and a switch to Cl chemistry after, the polar sunrise (during the ozone depletion events). The changes in ethyne concentration from their background level were in excess of those expected from Cl-atom kinetics alone and are attributed to additional Br-atom reactions. The time integral for Br mixing ratios is a few orders of magnitudes higher than that for Cl-atoms, suggesting much higher Br-atom concentrations compared to Cl-atom concentrations, if they are present simultaneously. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polar sunrise experiment 1995; Hydrocarbons; Chlorine; Bromine

## 1. Introduction

There are several reports of boundary layer tropospheric ozone depletions after the polar sunrise at various places in the Arctic (Barrie et al., 1988; Mickle et al.,

1989; Oltmans et al., 1989; Bottenheim et al., 1990; Anlauf et al., 1994; Barrie et al., 1994; Jobson et al., 1994; Solberg et al., 1994; Hopper et al., 1998; Ariya et al., 1998a). During these ozone depletion episodes, concurrent decreases in the concentration of hydrocarbons from their background levels have also been observed (Bottenheim et al., 1990; Jobson et al., 1994; Yokouchi et al., 1994; Muthuramu et al., 1994 and Ariya et al., 1998a). The observed changes in the hydrocarbon concentrations matched the kinetics of Cl-atom and Br-atom initiated reactions, implying the involvement of Cl- and Br-atoms in the destruction of hydrocarbons

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(Jobson et al., 1994; Ariya et al., 1998a). In addition, direct measurement of BrO (Hausmann and Platt, 1994), a product of Br-atom reaction with O<sub>3</sub>, indicated that halogens were not only responsible for hydrocarbon depletions but also react and deplete ozone (Jobson et al., 1994; Ariya et al., 1998a).

Polar Sunrise Experiment (PSE) 1995, the subject of this paper, is the second field campaign of its type in which hydrocarbon measurements have been made. By covering the period prior to, as well as during, the polar sunrise, this campaign provides information on distinctive hydrocarbon trends associated with the whole polar sunrise period. PSE 95 was particularly designed to verify that the depletions of some hydrocarbon species are reoccurring processes during the polar region. In addition, we aimed to confirm that hydrocarbon depletions occur concurrently with ozone destruction episodes. This paper reports measurements of C<sub>1</sub>–C<sub>7</sub> hydrocarbons at Alert between Julian days 57–113, 1995. It is the second campaign of its type, thereby making possible comparisons with the previous campaign (PSE 92). In addition, the intensive measurements during April provide a comparison with PSE 94 which focused mainly on the period after the sunrise. By using a wide range of hydrocarbons as indicators of photochemical processes, this study has attempted to evaluate the extent of halogen chemistry in the Arctic troposphere.

## 2. Experimental

Grab sampling was conducted outside the special studies laboratory at Alert from Julian days 57–113, 1995. In total 132 samples were taken at a frequency of at least once a day and up to six samples per day, with the exception of the period 21 February to 1 March, when only one sample was taken. Hourly averaged methane data were obtained at the Alert station using an automated GC/FID (Worthy et al., 1988). The details of experimental procedures for nonmethane hydrocarbon analysis are available elsewhere (Jobson, 1994). Air samples were collected in 3.2 L SUMMA electropolished stainless-steel canisters (Biospherics Research Corporation, Oregon) pressurized to 35 psig by means of a Teflon diaphragm pump (KNF Neuberger Incorporated). Replicate samples taken at Alert showed reproducibility of better than 5%. Canisters were returned to York University in Toronto for analysis. C<sub>2</sub>–C<sub>7</sub> hydrocarbons were measured using a gas chromatograph (GC) (Hewlett Packard 5890A) equipped with a flame ionization detector (FID) and a 50 m × 0.32 mm Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column. About 1 L of the air sample was preconcentrated using a two-stage cryotrapping procedure. Identification and quantification of NMHC species were made using reference gas mixtures blends (Conservation and

Protection Service, Environment Canada). The quantitation limits based on FID response and baseline noise were approximately 5 pptv for the C<sub>5</sub> hydrocarbons in a 1 L sample. Analytical precision for 1 L sample size and 100 pptv concentration was about ±1% for C<sub>2</sub>–C<sub>4</sub> alkanes.

## 3. Results and discussion

During PSE 95, the average air temperature observed at the beginning of the sampling period in the month of February was about 238 K and increased to about 258 K at the end of the study. Ozone mixing ratios dropped occasionally to less than 6 ppbv at the end of March and during April and sometimes below the detection limit of 0.5 ppbv. The maximum ozone mixing ratio between depletion events was approximately 50 ppbv. The 5 day back trajectories indicated that the air mass had traversed the ice-covered Arctic Ocean at least for one day. The interpretation of trajectories for depletion events is more complicated. As pointed out by Hopper et al. (1998), the complex topography of this region may contribute to errors in the calculation of trajectories.

### 3.1. Concentration-time series

Time series for the concentrations of the major C<sub>2</sub>–C<sub>7</sub> alkanes, toluene, ethyne, ethene, benzene are shown in Fig. 1a–f. The correlation coefficients (*r*) among most NMHCs were greater than 0.8, with the exception of benzene. Shown in Fig. 1a and b are the time series plots for selected hydrocarbons and ozone. All alkanes, toluene, and ethyne show a positive correlation with ozone. Benzene concentrations did not show a marked decline or recovery during low and high ozone episodes, but showed a slow decline from the beginning to the end of sampling period. Ethene concentrations were also measured but are not considered reliable, since an artifact was observed in the travelling blanks (Ariya et al., 1998a).

Fig. 2a shows the methane and ethane concentrations at Alert, and Fig. 2b shows the correlation between methane and ethane. During the dark period, methane correlated well with ethane and other alkanes. The correlation coefficient (*r*) for the plot shown in Fig. 2b is 0.824 with a slope of  $17.6 \pm 3.0$  ppbv/ppmv. This observation is consistent with the previous measurements by Jobson et al. (1994) who report similar correlation and slope values (*r* = 0.905, slope = 17.0) during the dark period in 1992. After the polar sunrise, there is no correlation (*r* < 0.1) between ethane and methane which suggests a change in the atmospheric processes controlling the NMHC mixing ratios at Alert around the time of sunrise.



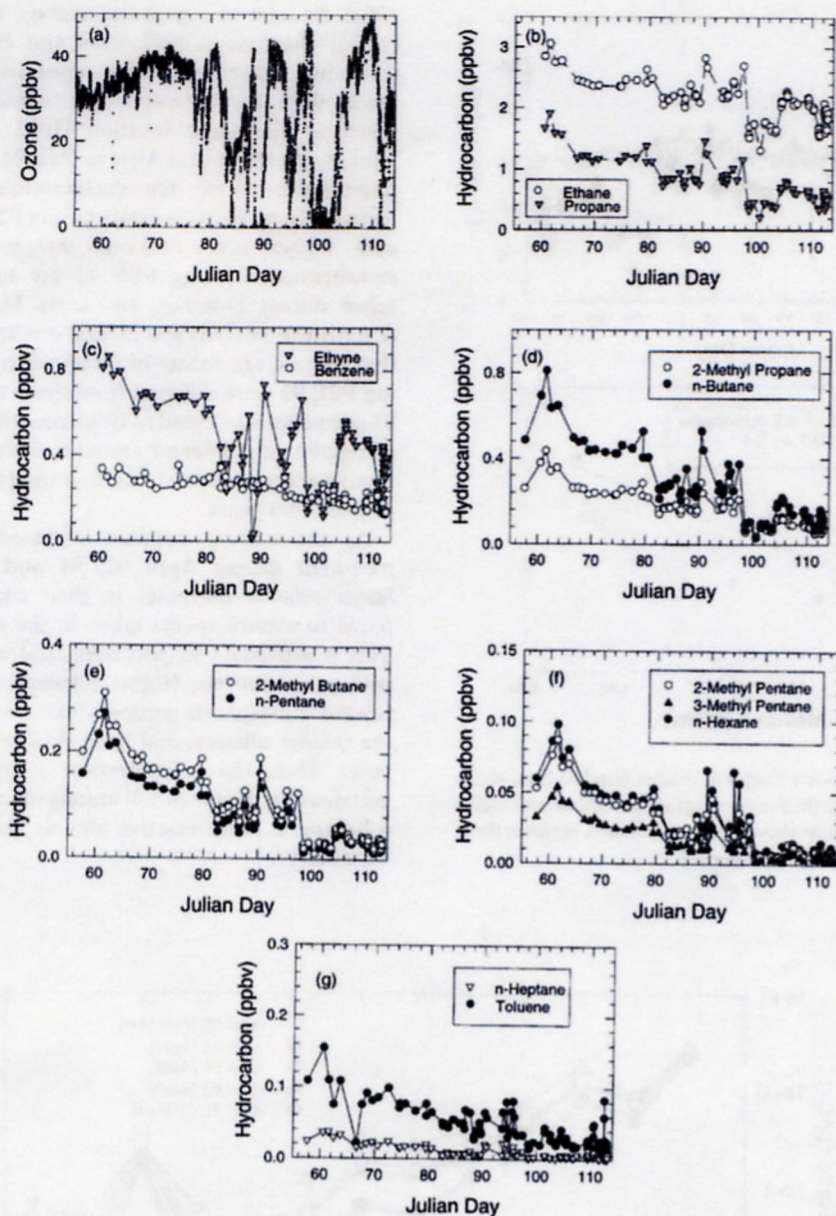


Fig. 1. Time series for some  $C_2$ – $C_7$  hydrocarbons at Alert (February–April 1995): (a) Ozone; (b) ethane, propane; (c) ethyne, benzene; (d) n-butane and 2-methyl propane; (e) n-pentane and 2-methyl butane; (f) n-hexane, 2-methyl pentane and 3-methyl pentane; (g) n-heptane and toluene.

### 3.2. Year-to-year variability in hydrocarbon distributions at alert

The average concentrations and relative distribution of  $C_2$ – $C_7$  hydrocarbons are compared to those measured previously at high-latitude northern hemisphere sites in

Fig. 3. In Fig. 3, average mixing ratios of hydrocarbons at Alert, during periods of “normal” ozone concentrations ( $O_3$  mixing ratio  $\geq 30$  ppbv) during February, March and April 1995 are compared to measurements made at the same site in 1994, and during winter (January and February) 1992 and spring (April) 1992 (Jobson et al.,

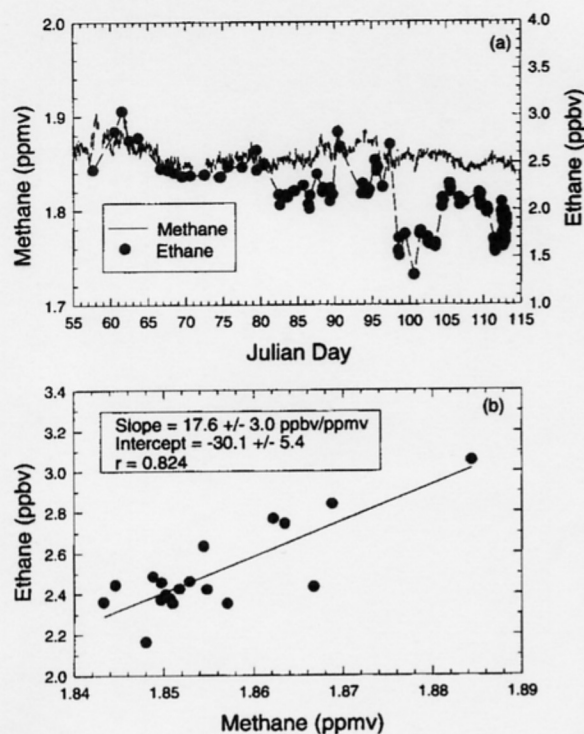


Fig. 2. (a) Methane (solid line) and ethane (circles) time series (February–April 1995); (b) Scatter diagram for ethane and methane prior to polar sunrise showing the correlation between these two molecules during the dark period.

1994). As seen in Fig. 3, the average values of alkanes ( $\geq C_3$ ) observed in 1992, 1994 and 1995 during April (excluding ozone depletion episodes) are markedly lower than the corresponding winter measurements taken at the same location (1992 and 1995). The April measurements at Alert in PSE 94 and 95 are indistinguishable within the uncertainties, but, for most hydrocarbons, measurements during PSE 92 show markedly higher concentrations. Moreover, the winter measurements during PSE 92 are higher than those taken during February and early March of PSE 95. A statistical analysis was carried out and the probability that the average values of measured hydrocarbons during PSE 92 were different from those taken during PSE 95 campaign was found to be greater than 0.99 indicative of significantly different amount of photochemical processing and/or source strengths during the winter periods of these two years.

As the carbon number increases in the alkanes measured during April 92, 94 and 95, we observe larger relative decreases in their concentration compared to measurements taken in the respective winters. This is attributed to photochemical activity associated with polar sunrise. Higher alkanes are more reactive toward atmospheric oxidants such as HO and Cl than the smaller alkanes, and have shorter atmospheric lifetimes. Thus, the concentration of ethane shows little variation ( $\leq$  factor of 1.4) among all measurements, but n-hexane, a more reactive alkane, shows much higher variability.

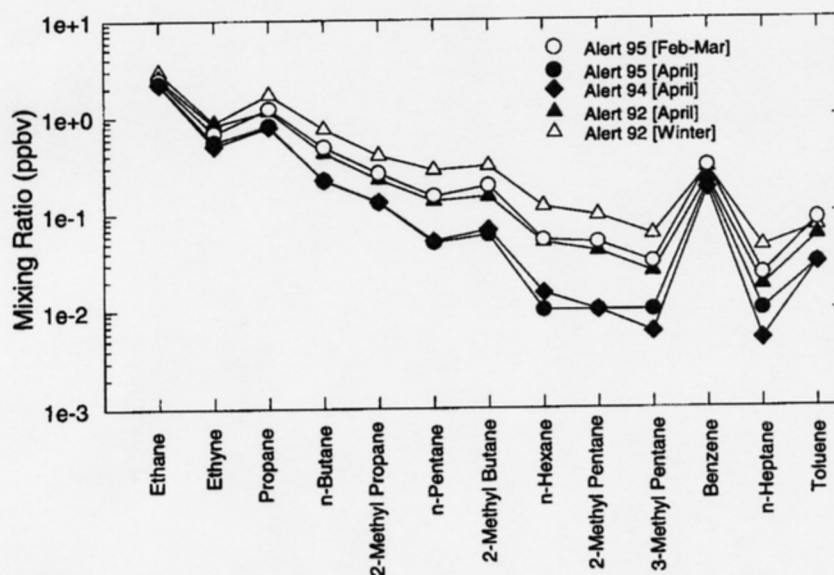


Fig. 3. (a) Comparison of average  $C_2$ – $C_7$  hydrocarbon concentrations at Alert 1995 and those taken during 1992 and 1994 at the same location. Concentrations are plotted on a log scale.



### 3.3. Hydrocarbon and ozone concentration changes and halogen chemistry

#### 3.3.1. Isomeric ratios and the distinction between HO and Cl chemistry

A clear distinction between Cl and HO initiated oxidation can be made by plotting the ratios [2-methyl propane]/[n-butane] vs. [2-methyl propane]/[propane] (Parrish et al. 1993; Jobson et al., 1994). For HO kinetics, the ratio of [2-methyl propane] to [n-butane] will remain constant while the [2-methyl propane] to [propane] ratio will decrease with processing time. In contrast, for Cl oxidation, the [2-methyl propane] to [n-butane] ratio will increase while the [2-methyl propane] to [propane] ratio remains constant. Therefore, in a plot such as Fig. 4a, pure HO kinetics will align data horizontally, while pure Cl-atom kinetics will align data vertically. The Alert 1995 data are plotted in this fashion in Fig. 4. The data from ozone depletion periods are consistent with a vertical trend, lying orthogonal to the data obtained during the high ozone events. As can be seen in Fig. 4b, this distinction between the HO and Cl kinetics is further indicated in plots of [2-methyl butane]/[n-pentane] vs. [2-methyl butane]/[n-butane].

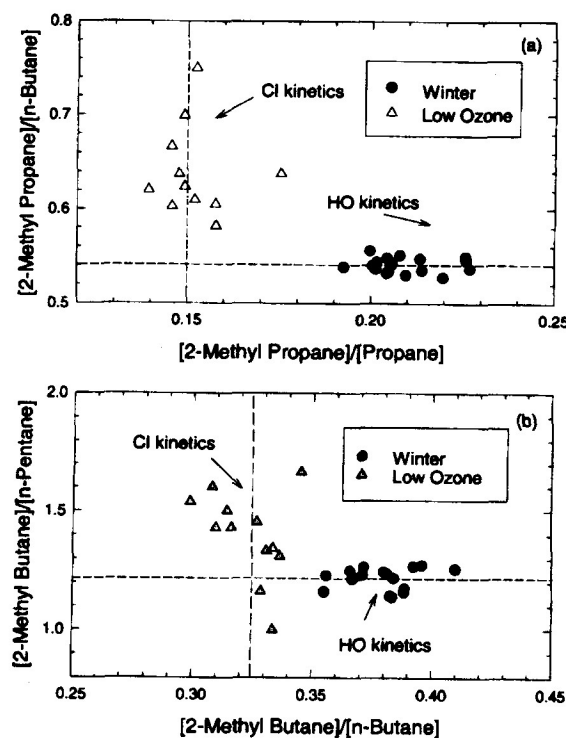


Fig. 4. (a) Plot of [2-methyl propane]/[n-butane] vs. [2-methyl propane]/[propane] at Alert. (b) Plot of [2-methyl butane]/[n-butane] vs. [2-methyl butane]/[n-pentane].

Various sources of NMHC contain different ratios of alkanes e.g. 2-methyl propane/n-butane ratios vary among various sources of natural gases, hence mixing of air masses from different sources could, in principle, give rise to various distributions which would complicate the above interpretation of hydrocarbon ratio plots in Fig. 4. However, we observed consistent behaviour in four sets of hydrocarbon ratios, thus the concentrations of five alkanes with different atmospheric lifetimes and temporal and spatial variation were consistent with HO chemistry in the wintertime and Cl chemistry during the ozone depleted events. Hence, it is reasonable to assume that the dominant factor leading to the behaviour illustrated in Fig. 4 is a switch from HO chemistry to Cl chemistry after the polar sunrise, during the ozone depletion events.

#### 3.3.2. Halogen atom chemistry during major ozone depletion events

We assume "background" concentrations for NMHCs when the ozone mixing ratio is at its normal levels ( $\geq 30$  ppbv). The change in concentration of a molecule from its "background" level  $[\text{Molecule}]_{\text{BKG}}$  to the concentration observed in ozone-depleted air,  $[\text{Molecule}]_{\text{Low}}$  can be related to Cl-atom reaction kinetics by the rate law expression,

$$[\text{Molecule}]_{\text{Low}} = [\text{Molecule}]_{\text{BKG}} \exp \left( -k_{\text{Cl}} \times [\text{Cl}] \, dt \right) \quad (1)$$

where  $k_{\text{Cl}}$  is the Cl-atom rate constant and  $[\text{Cl}]$  is the Cl-atom concentration. A plot of  $\ln([\text{Molecule}]_{\text{Low}}/[\text{Molecule}]_{\text{BKG}})$  vs.  $k_{\text{Cl}}$  should be linear with slope equal to the term  $-\int [\text{Cl}] \, dt$ . Table 1 shows Cl, HO and Br rate constants at 243 K for ozone and the NMHCs measured during this study. To account the daily variabilities in hydrocarbon mixing ratios, each background and low mixing ratios correspond to the average of at least two sets of samples taken prior and during ozone depletion events. Table 2 shows the results of the calculation of the above integral using these rate constants for a series of ozone depletion events at Alert. We carried out sensitivity tests for this kind of kinetic analysis using different data points taken during normal and depletion events. In the worse case, we observed a 40% deviation from the value reported in Table 2. Fig. 5 shows the log ratio plots for the two major depletion events at Alert, where the ozone mixing ratios dropped from its so-called background levels at this time of the year ( $\leq 30$  ppbv) to values close to our detection limit ( $< 5$  ppbv); note that the concentrations of ethyne during the ozone depletion events showed clear deviations from Cl-chemistry. As pointed out previously (e.g. Solberg et al., 1996) a strictly chemical model of the hydrocarbon trends will yield a lower limit on the actual halogen atom concentrations due to the effects of mixing. Thus, the

Table 1

Rate constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the reactions of measured hydrocarbons and ozone with HO, Cl- and Br-atom at 243 K

Molecule	HO	Cl	Br
Methane	$2.07 \times 10^{-15a}$	$3.71 \times 10^{-14c}$	$6.52 \times 10^{-26} / h$
Ethane	$1.18 \times 10^{-13a}$	$5.32 \times 10^{-11d}$	$2.32 \times 10^{-21} / h$
Ethane	$1.17 \times 10^{-11b}$	$9.29 \times 10^{-11ac}$	$1.09 \times 10^{-12i}$
Ethyne	$4.93 \times 10^{-13a}$	$8.44 \times 10^{-11d}$	$1.54 \times 10^{-13i}$
Propane	$7.45 \times 10^{-13a}$	$1.27 \times 10^{-10f}$	$1.31 \times 10^{-18} / h$
n-Butane	$1.92 \times 10^{-12a}$	$1.94 \times 10^{-10af}$	$1.86 \times 10^{-23} / k$
2-Methyl propane	$1.88 \times 10^{-12a}$	$1.30 \times 10^{-10af}$	$1.24 \times 10^{-16j}$
n-Pentane	$3.12 \times 10^{-12a}$	$2.50 \times 10^{-10af}$	
2-Methyl butane	$3.90 \times 10^{-12ab}$	$2.03 \times 10^{-10af}$	
n-Hexane		$3.05 \times 10^{-10af}$	
2-Methyl pentane		$2.58 \times 10^{-10af}$	
3-Methyl pentane		$2.58 \times 10^{-10af}$	
Benzene	$8.6 \times 10^{-13ab}$	$1 \times 10^{-12e}$	
Toluene	$6.19 \times 10^{-12ab}$	$5.6 \times 10^{-11*}$	
Ozone	$3.10 \times 10^{-14b}$	$9.55 \times 10^{-12g}$	$6.72 \times 10^{-13g}$

\* Room temperature.  $\infty$  Estimated.

a. Atkinson, 1992; b. Atkinson, 1986; c. 243 K value was obtained using room temperature data of Ariya and Niki, 1995 and suggestion of Atkinson et al., 1992; d. Ariya, Ph.D., 1996; e. Ariya et al., 1998b; f. Ariya and Niki, 1995; g. Nicovich et al., 1990; h. Russell et al., 1988a; i. Barnes et al., 1993; j. Russell et al., 1988b; k. Galiba, 1964.

Table 2

First-order regression data from plots of  $\ln([\text{Molecule}]_{\text{Low}}/[\text{Molecule}]_{\text{HKG}})$  vs.  $k_{\text{Cl}}$  for ozone depletion episodes alert

Episode	Slope: $-\int [\text{Cl}] dt$ (atoms $\text{cm}^{-3} \text{ s}$ )	Correlation coeff. ( $r^2$ )	y-intercept
Alert (JD 89, 95)	$-1.8 (\pm 0.6) \times 10^9$	0.89	$-0.04 \pm 0.06$
Alert (JD 100, 95)	$-7.1 (\pm 0.8) \times 10^9$	0.98	$0.07 \pm 0.14$

\*Stated uncertainties are two standard deviations. JD: Julian days.

halogen atom integrals determined in this way must be considered a lower limit.

To verify the selectivity of these kinds of kinetic plots, the hydrocarbon concentration changes for the Julian day 100 episode at Alert are plotted against HO rate constants at 243 K in Fig. 6. This plot makes it clear that the relative concentration changes are not related to the kinetics of HO removal. In Figs. 5 and 6, we did not include data for the higher alkanes ( $> \text{C}_5$ ) and toluene, because of poor precision since their concentrations during the ozone depletion events were close to or below the quantitation limit of our instrumentation.

### 3.3.3. The ratio of Cl and Br time action integrals

The deviation of ethyne from the least-squares fit to the  $\text{C}_2$ – $\text{C}_5$  alkanes, toluene and benzene may be a result of additional removal by Br-atoms (see Fig. 5).

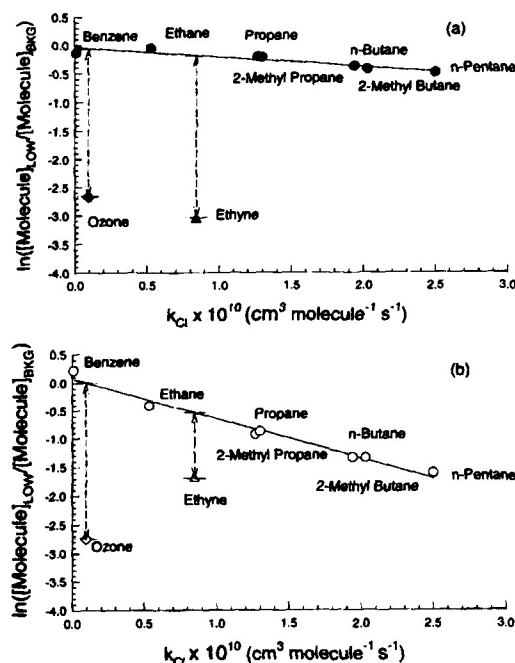


Fig. 5. (a) Hydrocarbon concentration change in ozone depleted air on JD 89, 1995 compared to normal ozone days plotted against  $\text{Cl} + \text{HC}$  rate constants. Least-squares fit line has been drawn through the data. (b) Similar plot for JD 100 1995.

Br-atom reactions have previously been invoked to explain the decreases in ethyne and ethene observed at Alert (Bottenheim et al., 1990; McConnell et al., 1992; Jobson et al., 1994). Eq. (2) describes the decrease in



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