Cation Transport in Low Density Ethene and Cyclopropane Gases

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Dedicated to Professor Schulte-Frohlinde on the occasion of his 60th anniversary

Cation mobilities were independent of applied electric field strength over the range $0.06 \leqq (E/n)/\mathrm{Td} \leqq 25$ in ethene, and $0.07 \leqq (E/n)/\mathrm{Td} \leqq 81$ in cyclopropane. In the saturated vapors the density normalized mobility $n\mu_+$ was independent of vapor density over the range $0.2 \lesssim n/10^{25}$ molec $\mathrm{m}^{-3} \lesssim 80$; $n\mu_+ = (1.95 \pm 0.09)/10^{21}$ molec $\mathrm{m}^{-1}\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ in ethene and $(1.43 \pm 0.07)/10^{21}$ molec $\mathrm{m}^{-1}\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ in cyclopropane. The constancy was caused by the virtual cancellation of small temperature and density effects. In the nonsaturated gases at constant density the temperature coefficient $n\mu_+$ was positive at 200 K, but decreased to near zero at 600 K. The momentum transfer cross sections σ_m were dominated by ion-induced dipole interactions at $0.06 \lesssim \varepsilon/\mathrm{eV} \lesssim 0.2$. At lower energies a softer potential, such as ion-quadrupole, made a major contribution, while at higher energies the hard core potential contributed significantly.

I. Introduction

The understanding of charge transport in hydrocarbon fluids requires information about electron and cation behavior in fluids at all densities, from that of the dilute gas to that of the normal liquid. Cation mobilities have been measured in simple hydrocarbons over the entire liquid range and in the supercritical fluid [1 – 4], and in the dense gas [2 – 5]. The behavior in low density gases is now being studied to obtain ion-molecule scattering cross sections.

The first gas to be reported, ethene, generates multimeric cations in the radiolysis measuring system [6, 7], so effects of additional molecular clustering on the ion are negligible. The reduced mass of the ion-molecule collisions is nearly equal to the molecular mass. The second gas, cyclopropane, would also generate multimeric cations by way of the trace of propene that it contains.

The ion-molecule collision energy in inorganic systems has usually been varied by applying sufficiently high electric field strengths [8 – 10]. In the present work the energy was varied by changing the temperature over a wide range.

II. Experimental

A) Materials

Research grade ethene (Phillips Petroleum, 99.97%) and cyclopropane (Matheson, 99.3%, with 0.3% propene and 0.4% air) were further purified in a grease free vacuum line. Trap to trap distillations while pumping on the liquid nitrogen cooled receiver were followed by treatment of the gases at room temperature with potassium mirrors for a period of at least one month. The mirrors were renewed at least four times for each sample. The samples showed no change with time over a one year period in contact with the mirrors.

B) Conductance cells

Most of the cells were similar to that described in [11]. They had drift distances in the range 2.62 to 10.0 mm.

One series of cyclopropane saturated vapors that extended to 0.7 MPa was done in a high pressure cell similar to that described in [12]. The drift distance was 3.20 mm.

C) Temperature measurement and control

The temperature of the cell was lowered by blowing cold nitrogen gas on the cell in a Styrofoam

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box, and elevated by blowing hot air on the cell in a silvered dewar. The temperature of the cell was monitored at four points (top, 2 sides at the level of the plates, and bottom), with type *T* special copper-constantan thermocouples (Thermoelectric Co.) and a Fluke 2100A digital thermometer. The maximum difference between readings at the four points at $T < 294$ K was typically < 0.5 K, although extremes of ~ 2 K occurred. At $T > 294$ K the difference was less than 1%, with 0% at $T \sim 294$ K and increasing towards 1% at ~ 600 K. The temperature of the cooling nitrogen gas or of the air from the heat gun was controlled by a platinum thin film detector (Omega Engineering) near the body of the cell, connected to a Taylor Micro Scan 1300.

D) Voltage

Positive and negative voltages were applied to the plates of the conductance cells using a Fluke 4088 High Voltage Power Supply. The applied voltage was measured with a Fluke 8810A multimeter to < 0.5%.

E) Mobility measurement

The ions were produced in the gas by a 100 ns pulse of X-rays which delivered a dose at $\sim 6 \times 10^{10}$ eV/g. The [ion]/[molecule] ratio in the sample was $\sim 10^{-13}$. The mobilities were determined by a time of flight method. The electrons were swept from between the electrodes of the cell in a period of microseconds, and the ions were swept out in milliseconds by the same field. Data collection was controlled by a Texas Instruments 980A minicomputer. The induced current was amplified with a Princeton Applied Research 113 preamplifier. The signal was stored in a Nicolet Instrument 1170 signal averager prior to printing on a Zeta Research 1200 plotter.

A sample trace with the drift time t_d marked on it is shown in Figure 1.

F) Physical properties

Densities for ethene are readily available [13]. Cyclopropane vapor densities measured at $T \geqq 320$ K [14] agree with values previously estimated [15] from a combination of the Van der Waals equation [16] and the law of rectilinear diameters. At $293 \leqq T/\mathrm{K} \leqq 342$, that is up to 2 MPa, cyclopropane densities calculated by the Van der Waals equation were ~ 4% less than those in [14]. At $T \leqq 240$ K the present work used densities calculated by the Van der Waals equation using vapor pressures from [17] and multiplied by 1.04. Densities at $240 \leqq T/\mathrm{K} \leqq 293$ were obtained by smooth interpolation.

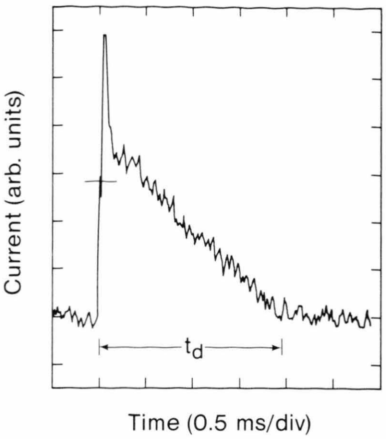

Fig. 1. Current-time trace for cations in cyclopropane at $n = 1.48 \times 10^{25}$ molec/m^3, $T = 294$ K, $V = 100$ volts, drift distance = 4.80 mm.

G) Thermal decomposition of the hydrocarbons and outgassing of the cells

The possibility of thermal decomposition at $T > 590$ K was examined by: (1) measuring both the electron and ion mobilities at $T \approx 294$ K, (2) heating to a temperature > 590 K and measuring both mobilities, (3) cooling to $T \approx 294$ K and remeasuring both mobilities. Replication of both mobilities was taken to demonstrate absence of significant thermal decomposition of the sample or of outgassing from the metal plates. The present data were free from these effects at $T < 650$ K. Decomposition became important at 660 K in ethene and 654 K in cyclopropane.

III. Results and Discussion

A) Field independence

The cation mobility was independent of applied E/n over the range 0.06 to 25 Td ($1\ \mathrm{Td} = 10^{-21}\ \mathrm{V \cdot m^2/molec}$) for ethene and 0.07 to 81 Td for cyclopropane. Both positive and negative voltages were applied; no voltage polarity effect was identified.

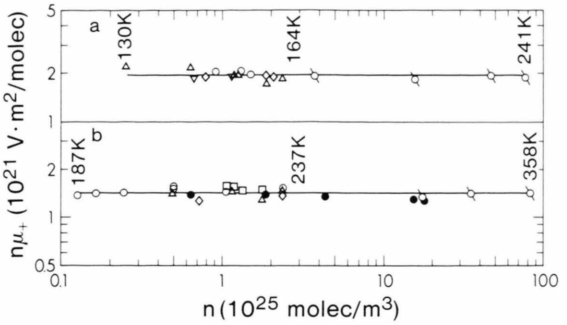

Fig. 2. Density dependence of $n\mu_+$ in saturated vapors of ethene (a) and cyclopropane (b). The symbols indicate cell drift distances/mm: a) ◇ (2.62), △ (4.80), ▽ (8.9), ○ (10.0), ꝗ (3.20, Ref. [5]); b) as in (a) except ● (3.20) and □ (7.27).

Normally, at each density and temperature, more than 10 measurements at fields ~ 1 to 10 Td were used to calculate an average mobility; the average deviation from the mean was usually 2 – 3%.

B) Saturated gas

At low gas densities n and very low ion mole fractions the product $n\mu_+$ is independent of n [18]. The present results in the saturated vapors of ethene and cyclopropane show that $n\mu_+$ is independent, within ± 5%, of density over the range 0.2 – 80 (10^{25} molec/m^3) (Figure 2). The average of the fourteen new $n\mu_+$ values in saturated ethene vapor is (1.95 ± 0.09) 10^{21} molec m^{-1} V^{-1} s^{-1}, and of the twenty two new values in cyclopropane is (1.43 ± 0.07) 10^{21} molec · m^{-1} V^{-1} s^{-1}.

C) Nonsaturated gas

The conductance cells were sealed with a flame after the samples had been condensed into them at 77 K. For each filling the gas density was fixed, independent of temperature change during the series of measurements.

The mobility increased with temperature in both gases (Figure 3). The relative temperature coefficient $(n\mu_+)^{-1}\,(\mathrm{d}n\mu_+/\mathrm{d}T)$ at 200 K was 2.4×10^{-3} K^{-1} in ethene and 2.9×10^{-3} K^{-1} in cyclopropane. The coefficients decreased with temperature and were 10 fold smaller, or essentially zero, at 600 K in each gas. The density normalized mobilities $n\mu_+$ depended only on T, not on n, in the density range 1 – 3 (10^{25} molec/m^3). The mobilities were therefore not affected by changes in extent of clustering that might have occurred with changing temperature.

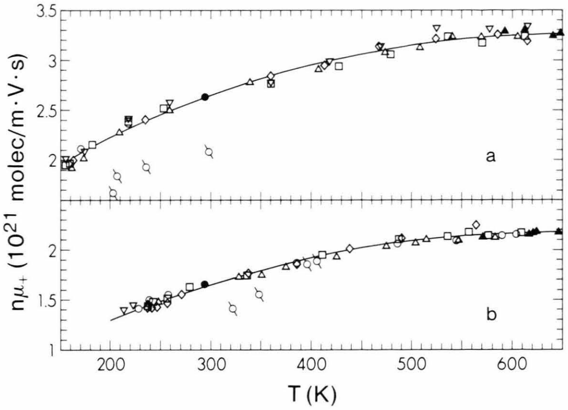

Fig. 3. Temperature dependence of $n\mu_+$ in nonsaturated gases of ethene (a) and cyclopropane (b). The symbols indicate (drift distance/mm, density/10^{25} molec/m^3). a) ◇ (2.62, 2.73), ▲ (4.80, 1.62), △ (4.80, 2.64), □ (4.80, 1.44), ▽ (8.9, 1.65), ○ (10.0, 1.76), ꝗ (3.20, 18.9, Ref. [5]). b) ◇ (2.62, 2.86), △ (4.80, 2.53), ▲ (4.80, 1.48), □ (7.27, 2.35), ○ (10.0, 1.45), ▽ (10.0, 0.64) and ꝗ (3.20, 35.1, Ref. [5]). ● represents the average value at 294 ± 1 K at all densities. Each set was normalized to this value to remove the ± 2.3% (ethene) and ± 3.0% (cyclopropane) random scatter produced by uncertainties in the gas densities and cell dimensions. The lines were calculated from (1), using cross sections from Figure 4a.

The values of $n\mu_+$ from [5] were lower than the present ones because they were obtained at much higher densities (Figure 3). In the coexistence vapor $n\mu_+$ is essentially independent of n (Fig. 2), but T and n increase concomitantly. The n and T effects cancel each other, within the experimental uncertainty.

D) Momentum transfer cross sections

Momentum transfer cross sections σ_m in the low density gases were deduced by fitting (1) [8] to the data in Figure 3.

$$n\mu_+ = \frac{3e\sqrt{\pi}}{8M_\mathrm{r}}\left(\frac{2kT}{M_\mathrm{r}}\right)^{5/2} \Big/ \int_0^\infty v^5\,\sigma_\mathrm{m} \exp\left(\frac{-M_\mathrm{r}v^2}{2kT}\right) \mathrm{d}v\,, \tag{1a}$$

$$= \frac{3e}{8}\,(kT)^{5/2}\left(\frac{2\pi}{M_\mathrm{r}}\right)^{1/2} \Big/ \int_0^\infty \varepsilon^2\,\sigma_\mathrm{m} \exp\left(-\frac{\varepsilon}{kT}\right) \mathrm{d}\varepsilon\,, \tag{1b}$$

where M_r is the ion-molecule reduced mass, v is the relative velocity of the ion with respect to the molecule and $\varepsilon = M_\mathrm{r}v^2/2$. The cross sections decrease with increasing energy, but have a somewhat more complex energy dependence that predicted from the

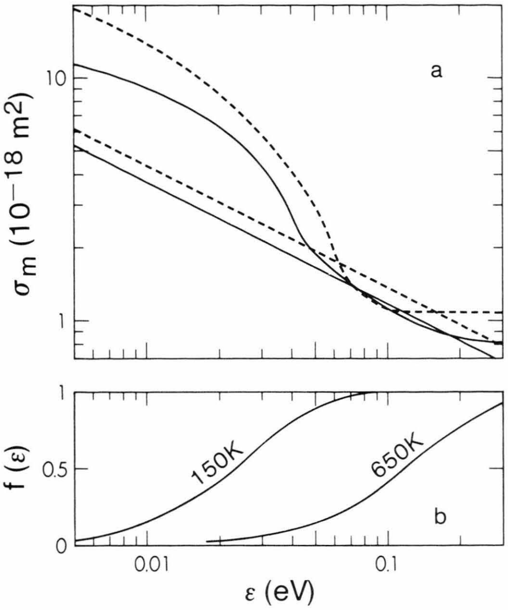

Fig. 4a). Cation momentum transfer cross sections σ_m of ethene (——) and cyclopropane (---). The curves were estimated by fitting (1) to the measured mobilities in Fig. 3, using $M_r = 0.9$ X molecular mass. The straight lines represent σ_{pol}, Equation (2). b) $f(\varepsilon)$, the fraction of the integral in (1) that has been contributed by integration from zero to ε, for ethene at 150 and 650 K.

simple polarization potential (Figure 4a). The latter cross sections σ_{pol} are given by (19):

$$\sigma_{pol} = (2.2\pi e/v)\,(\alpha/M_r)^{1/2}, \qquad (2a)$$

$$\sigma_{pol}/m^2 = 1.86 \times 10^{-19}\,(\alpha/\varepsilon)^{1/2}, \qquad (2b)$$

where in (2b) the average polarizability α of the molecule is in units of 10^{-30} m^3 and the relative kinetic energy ε of the ion-molecule colliding pair is in eV. For ethene, $\alpha = 4.0 \times 10^{-30}$ m^3 [20] and one obtains $\sigma_{pol} = 3.7 \times 10^{-19}\,\varepsilon^{-1/2}$ m^2. For cyclopropane, $\alpha = 5.5 \times 10^{-30}$ m^3 [21] which gives $\sigma_{pol} = 4.4 \times 10^{-19}\,\varepsilon^{-1/2}$ m^2.

The cations in ethene irradiated at 10^{23} to 10^{24} molec/m^3 and ~ 300 K are polymeric and have masses up to that of the octamer [6, 7]. For lack of better information at higher gas densities we have assumed decamers, whence $M_r \approx 0.9$ times molecular mass. In cyclopropane we assumed that the cations were propene decamers. The essential point is that M_r did not appear to change appreciably with temperature or gas density in this region.

The procedure of fitting (1) to the data is most sensitive to changes in σ_m in the energy region between $f(\varepsilon) = 0.1$ and 0.9 (Figure 4b). In the present work this corresponds to $0.014 \lesssim \varepsilon/\text{eV} \lesssim 0.19$.

The values of σ_m are similar to those of σ_{pol} at ~ 0.1 eV, but σ_m increases more rapidly at low energies. The behavior is the opposite of that expected from a hard core contribution to the scattering potential [22]. The lack of density dependence of the mobilities indicates that the increase of σ_m is not due to an increase in M_r. The behavior is similar to that reported for CO_3^- collisions with N_2 [5], where the ions were calculated and mass identified (9a).

For a potential of the form

$$V(r) = \pm\, C r^{-p}, \qquad (3)$$

where C and p are positive constants, the energy dependence of the cross section is [23]

$$\sigma_m \propto (C/\varepsilon)^{2/p}. \qquad (4)$$

The ion-induced dipole potential varies as r^{-4}, which produces the $\varepsilon^{-1/2}$ dependence of σ_{pol} in (2b). At $\varepsilon < 0.07$ eV the values of σ_m vary more rapidly than $\varepsilon^{1/2}$ (Figure 4a), which means that the scattering potential is softer than r^{-4}. Ion-quadrupole potentials vary as r^{-3}, which would give $\sigma_{iq} \propto \varepsilon^{-2/3}$ according to the simple model. Ethene, cyclopropane and nitrogen have electric quadrupole moments. The rotationally averaged values are respectively, in units of 10^{-40} C · m^2, 5.0, 7 and 5.1 [24]. Although the energy dependence of σ_m is more complex than a simple power function (Fig. 4a), the relative magnitude of σ_m for the cations in ethene and cyclopropane at $\varepsilon < 0.05$ eV are consistent with the relative magnitudes of the quadrupole moments. The cross sections for CO_3^- in N_2 [5] are a factor of two lower than those in ethene, but the ethene multimeric cations are larger than CO_3^-.

At $\varepsilon > 0.1$ eV, σ_m is nearly independent of ε (Figure 4a and [8] Figure 10). At these energies σ_m is apparently reduced to a hard core contribution.

E) Average cross sections σ_{av}

Cross section curves such as those in Fig. 4a contain a degree of subjectivity, especially at the high and low energy ends. It is useful to record the temperature dependence of σ_{av}.

Equation (1) can be rewritten in terms of the average velocity $\langle v \rangle$ and σ_{av} [25].

$$n\mu_+ = (3e/4M_r)/\langle v \rangle\,\sigma_{av}, \qquad (5)$$

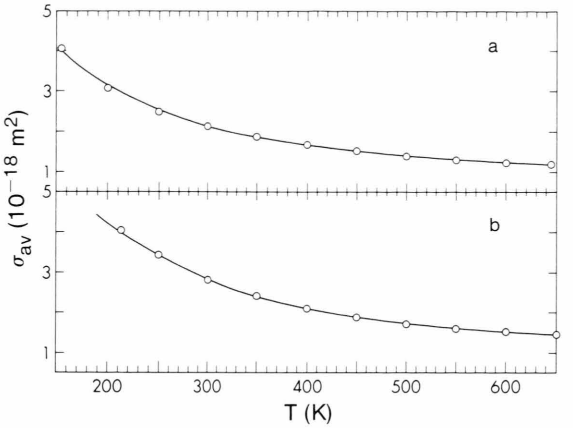

Fig. 5. Average cross sections σ_{av} of ethene (a) and cyclopropane (b) for scattering cations. Smoothed values of $n\mu_+$ from Fig. 3a and $M_r = 0.9$ X molecular mass were used in (5). The solid curves were calculated using the data in Fig. 4a and (6).

where

$$\sigma_{av} = \langle v^3 \sigma_m \rangle / \langle v^3 \rangle = \langle \varepsilon^{3/2} \sigma_m \rangle / \langle \varepsilon^{3/2} \rangle , \qquad (6)$$

and

$$\langle v \rangle = (8kT/\pi M_r)^{1/2} \qquad (7)$$

for a Maxwellian distribution of velocities.

Values of σ_{av} decrease monotonically with increasing temperature in both gases (Figure 5).

Summary

Cyclopropane, ethene and nitrogen all have moderately large quadrupole moments. The ion momentum transfer cross section σ_m of each of these molecules has a major contribution from a relatively soft potential such as ion-quadrupole (r^{-3}) at energies $\varepsilon < 0.06$ eV. At higher energies the dominant scattering potential becomes progessively harder. At $0.06 \lesssim \varepsilon/\mathrm{eV} \lesssim 0.2$ it is ion-induced dipole (r^{-4}), and at ~ 0.3 eV it is essentially hard core $(r^{-\infty})$ within the present sensitivity of measurement.

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