

Electron Mobility in Liquid Alkenes under High Pressure

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The mobility of excess electrons in 1-pentene, cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene has been measured as a function of pressure from 1 to 3000 bar and as a function of temperature. The volume changes associated with trapping of the electron in these alkenes are derived assuming an equilibrium exists between quasi-free and trapped electrons. The volume of trapping is positive or negative, depending on the magnitude of the electrostriction term relative to the cavity term. The entropy of trapping is small. A dependence of volume change on the compressibility of the liquid is shown.

Introduction

Monoalkenes as a class of hydrocarbon liquids exhibit a range of mobilities of excess electrons depending on the molecular structure. In methyl-substituted alkenes the mobility is typically high, and in linear or cyclic alkenes the mobility is low. In the two-state model the magnitude of the mobility is attributed to the position of the equilibrium:



depending on whether the electron is trapped (tr) or in a conducting (qf) state. The conduction band energy, V_0 , is an important factor that determines which state is favorable. This energy is known for only a few alkenes. For 2,3-dimethyl-2-butene, V_0 is -0.25 eV,¹ which favors the electron being quasi-free. In linear alkenes the conduction band will presumably be higher, favoring the trap state because of a higher activation energy required to return to the quasi-free state. The present study of the effect of pressure on the mobility further tests the applicability of this two-state model and derives additional information about electron traps.

The alkenes chosen for study exhibit a range of isothermal compressibilities χ_T , which provides an opportunity to test the recently reported effect of the magnitude of χ_T on the way pressure affects the mobility.² In alkane liquids the compressibility is generally quite large, and it has been observed that the electron mobility decreases with increasing pressure for *n*-alkane liquids.^{3,4} These decreases are interpreted as a negative volume change for reaction 1. In contrast, for *o*- and *m*-xylene, which are much less compressible, the electron mobility increases with increasing pressure. For these liquids the derived volume change of trapping is positive. To account for this difference, it was proposed² that the volume change in reaction 1 includes a cavity volume V_{cav} , which is always positive, and an electrostriction term V_{el} , which is negative. The latter is proportional to χ_T in the classical model;⁵ thus, the sign of the volume change in reaction 1 depends on the magnitude of χ_T .

Here, we report the effect of pressure on the electron mobility in 1-pentene, cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. The volume and entropy changes associated with trapping, reaction 1, are derived from the results.

Experimental Section

Mobilities were determined by the time-of-flight method as described earlier.⁶ That is, the conductivity of the sample following the pulse of X-rays, obtained by using a 2 MeV van de Graaff accelerator, was measured and analyzed.

Samples of 1-pentene (Aldrich 99%) and 2,3-dimethyl-2-butene were purified by first washing with milli-Q water and drying over molecular sieves. Then the samples were introduced into the vacuum line, degassed while frozen at -196 °C, passed through a column packed with silica gel and molecular sieves (4A), and finally stored over NaK alloy. This procedure had to be altered for 2-methyl-2-butene (Aldrich 99%), which when frozen at -196 °C undergoes charge separation, resulting in the emission of flashes of light. This electrification⁷ and accompanying sparking causes isomerization and reactions of the alkene. One such sample of 2-methyl-2-butene, which initially contained less than 1% of isomer and other impurities, was found by GC/MS analysis to contain 22% of another pentene isomer and 3% dimers after freezing. Degassing of the sample at a temperature above its melting point (-124 °C) avoided the sparking and provided a sample pure enough for use.

Samples of cyclohexene were obtained from both Aldrich (99+%) and Wiley (99.8%) and designated A and B, respectively. The UV spectra showed that sample A initially contained 1,3-cyclohexadiene (6 mM), which had to be removed because conjugated diolefins trap electrons.^{8,9} Sample B contained much less 1,3-cyclohexadiene (~ 0.2 mM). Both samples were purified in the usual manner, which removed the 1,3-cyclohexadiene. After the final NaK treatment, UV spectral analysis showed that sample A contained 24 mM benzene, which was

TABLE 1: Physical Properties of Alkenes

liquid	temp (°C)	density (g/cm ³)	ε	χ _T (×10 ⁻⁴ bar ⁻¹)	α (×10 ⁻⁴ K ⁻¹)	α/χ _T (cal K ⁻¹ cm ⁻³)
1-pentene	0	0.663	2.069	1.65 ^a	15.6	0.226
	20	0.641	2.011	2.37	16.1	0.162
	40	0.622	1.972	2.81, 2.58 ^a	16.6	0.141
	60	0.601	1.929	3.43	17.2	0.12
	80	0.572	1.870	4.40, 4.47 ^a	17.8	0.097
cyclohexene	10	0.823	2.253	0.691	12.0	0.415
	20	0.813	2.232	0.75, 0.88 ^b	12.2	0.389
	40	0.759				
	50	0.784	2.170	0.99	12.6	0.304
	75	0.759	2.119	1.215	13.05	0.257
2-methyl-2-butene	0	0.684	2.031	1.30 ^b	15.5	0.285
	20	0.662 ^c	1.986 ^d	1.63 ^b	16.1	0.236
	40	0.641	1.949 ^e	2.04 ^b	16.5	0.193
	60	0.620	1.909 ^e	2.58 ^b	17.1	0.159
	80	0.599	1.869 ^e	3.29	17.7	0.129
2,3-dimethyl-2-butene	20	0.708 ^f	1.984 ^g	1.12 ^b	13.0	0.278

^a Reference 16. ^b Based on ref 17. ^c Reference 18. ^d Reference 19. ^e Assumed Clausius–Mosotti equation. ^f Reference 20. ^g Reference 21.

not present initially. We suspect this was formed from an (undetected) 1,4-cyclohexadiene impurity, which is reported to react with NaK to form benzene.¹⁰ Sample B contained less benzene (<2 mM) after treatment. Although benzene traps electrons in alkanes at high pressure,¹¹ sample B was sufficiently pure and was used for mobility measurements.

Density data as a function of pressure for 1-pentene¹² and cyclohexene¹³ were fit to a Tait equation to derive compressibilities. The temperature dependence of density for 1-pentene is given by¹⁴

$$d(\text{g/cm}^3) = 0.663 - 0.001034t \quad (t \text{ in } ^\circ\text{C}) \quad (2)$$

A similar equation

$$d = 0.833 - 9.903 \times 10^{-4}t \quad (3)$$

was derived for cyclohexene by fitting the density data at 1 bar. Equation 4 was derived for 2-methyl-2-butene on the basis of published density data:¹⁵

$$d = 0.6835 - 0.00106t \quad (4)$$

Table 1 shows density (d), dielectric constant (ϵ), compressibility (χ_T), and thermal expansion coefficient (α) data for the experimental conditions of interest. The compressibilities of 2-methyl-2-butene and 2,3-dimethyl-2-butene are estimated on the basis of a dependence on molar volume given by Wada.¹⁷

Results

Figure 1 shows the pressure and temperature dependence of the electron mobility (μ) for 1-pentene. The mobility at 20 °C and 1 bar, $0.048 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, compares well with the value of μ for 1-butene, which is $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 267 K.²¹ The mobility increases with temperature and decreases with pressure up to high pressures where the mobility increases. Aside from the high-pressure increase, the effect of pressure on μ is very similar to that observed for *n*-pentane.⁴

Figure 2 shows the mobility observed for sample B of cyclohexene. At 1 bar and 20 °C the observed mobility is $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The value reported by Freeman is $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 23 °C.²⁰ Sample B was found to be the purest, and the mobility increases with pressure at all temperatures except the highest. Above 150 MPa the mobility decreases at 10 and 20 °C. This decrease is attributed to trapping by impurities and was much more significant in sample A, where it was clearly

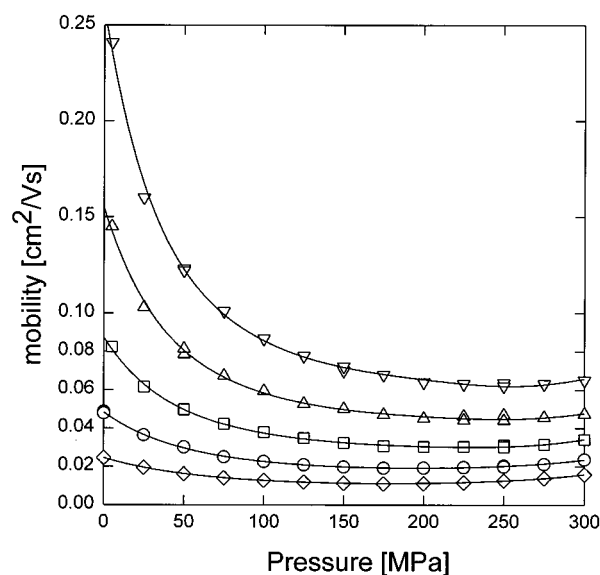


Figure 1. Electron mobility in 1-pentane as a function of pressure: 0 °C (◇); 20 °C (○); 40 °C (□); 60 °C (△); 80 °C (▽). Lines are least-squares polynomial fits to data.

observable at 25 MPa. At 20 °C the mobility in sample A was $5.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 200 MPa, close to that expected for ions.²² The mobility drops, we believe, owing to an equilibrium reaction with impurities. For example, benzene is present and is known to reversibly trap electrons at high pressures.¹¹ Conjugated diolefins do the same at low pressures.^{8,9}

In 2-methyl-2-butene (Figure 3) the mobility is $2.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 1 bar and 20 °C and changes little with pressure. The 1 bar value agrees with the value of $2.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 22 °C, reported by Dodelet et al.,²³ but is lower than an early value of $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 27 °C.²⁴ The mobility for this alkene is significantly higher than that of the analogous saturated alkane, 2-methylbutane, for which $\mu = 0.73 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 25 °C.²⁵ The dependence of the mobility on pressure is different also. In 2-methylbutane the mobility decreases with increasing pressures at all temperatures from 11 to 100 °C. In 2-methyl-2-butene the mobility decreases with pressure only at the higher temperatures.

In 2,3-dimethyl-2-butene the mobility increases slightly at all temperatures studied (Figure 4) except at 80 °C where the change is slight. The curves in Figure 4 converge at high pressure. The mobility at 1 bar and 20 °C is $8.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$;

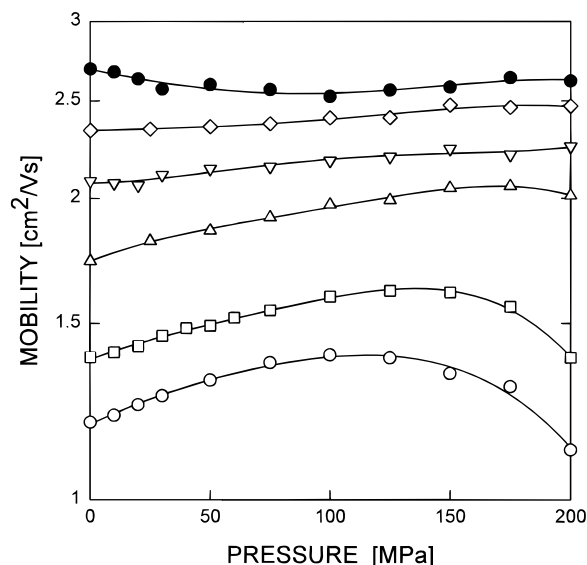


Figure 2. Electron mobility in cyclohexene as a function of pressure: 10 °C (○); 20 °C (□); 35 °C (Δ); 50 °C (▽); 60 °C (◇); 75 °C (●). Lines are fourth-order regressions through data.

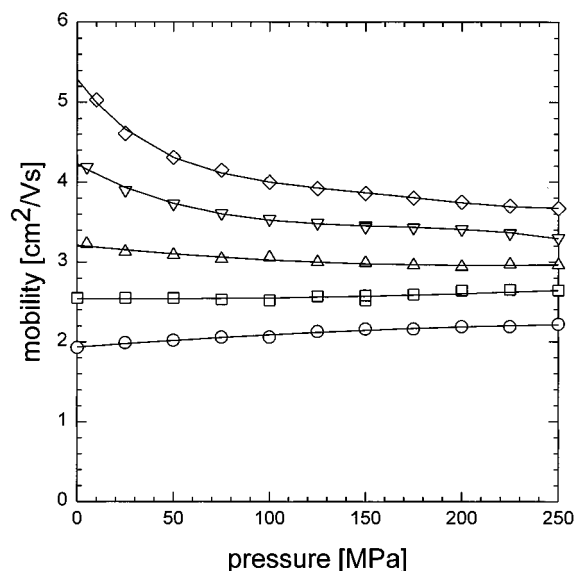
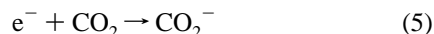


Figure 3. Electron mobility in 2-methyl-2-butene as a function of pressure: 0 °C (○); 20 °C (□); 40 °C (Δ); 60 °C (▽); 80 °C (◇). Lines are fourth-order regressions through data.

Dodelet et al. reported $5.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²³ Again, for this alkene the mobility is significantly higher than that for the saturated analogue 2,3-dimethylbutane, which is $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²¹ Addition of CO_2 to this alkene indicated it reacted with the fast transient, verifying it to be the electron.



The rate constant for reaction 5 in this alkene is $3.2 \times 10^{12} \text{ m}^{-1} \text{ s}^{-1}$ at 23 °C. Very comparable values were reported for this rate constant in 2-methylbutane²⁴ and 3-methylpentane.²⁶

Discussion

Volume Changes. Pressure affects the mobility by shifting the equilibrium, eq 1, either to the left or to the right, depending on whether the volume change for trapping is positive or negative. In the two-state model, the mobility is given by the mobility in the conduction band, μ_{qf} , times the fraction of

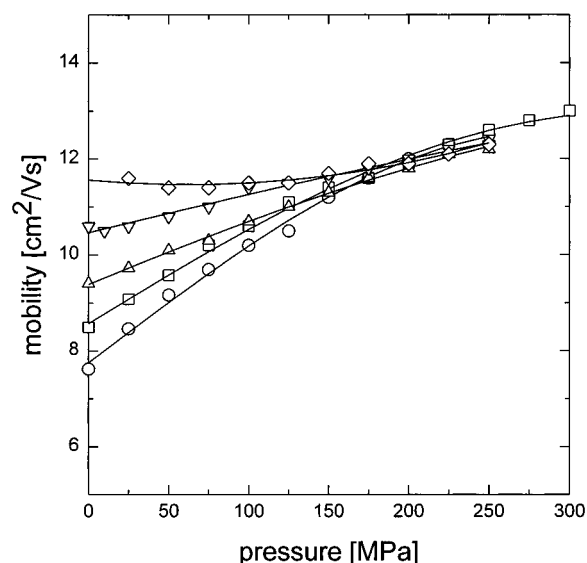


Figure 4. Electron mobility in 2,3-dimethyl-2-butene: 0 °C (○); 20 °C (□); 40 °C (Δ); 60 °C (▽); 80 °C (◇). Lines are quadratic fits to data.

electrons in that state: $[\text{e}_{\text{qf}}^-]/([\text{e}_{\text{qf}}^-] + [\text{e}_{\text{tr}}^-])$. Equivalently, the equilibrium constant for reaction 1, K_1 , can be written as

$$K_1 = (\mu_{\text{qf}} - \mu)/\mu \approx \mu_{\text{qf}}/\mu \quad (6)$$

since μ_{qf} is much larger than μ . The volume change associated with trapping then becomes

$$\Delta V = \frac{-RT \text{ d ln } K}{\text{d} P} = \frac{RT \text{ d ln } \mu}{\text{d} P} \quad (7)$$

assuming that μ_{qf} is independent of pressure between 0.1 and 300 MPa. This assumption is supported by data on high-mobility liquids such as tetramethylsilane^{3,6} and bis(trimethylsilyl)methane.²⁷ Mobility data versus pressure were fit to a polynomial of second to fourth order to evaluate the derivative in eq 7.

Resulting values of ΔV_1 for the alkenes are shown in Tables 2 and 3. For 1-pentene ΔV_1 is always negative at low pressures. At low pressures, ΔV_1 for cyclohexene is positive at low temperatures and becomes negative at 75 °C. Only the low-pressure (1 bar) data are shown for cyclohexene in Table 2, since impurities affect the data at high pressure. For 2-methyl-2-butene, ΔV_1 changes similarly from positive to negative as the temperature increases. The volume change calculated for 2,3-dimethylbutene is small and positive under most conditions.

Since both positive and negative volume changes are observed, and since electrostriction contributes only a negative volume change, these results support the interpretation²⁸ that the volume change for trapping includes a cavity volume, which is a positive term in eq 8.

$$\Delta V_1 = \bar{V}(\text{e}_{\text{tr}}^-) - \bar{V}(\text{e}_{\text{qf}}^-) = V_{\text{el}} + V_{\text{cav}} - \bar{V}(\text{e}_{\text{qf}}^-) \quad (8)$$

In previous papers^{2,28} the volume change in reaction 1, ΔV_1 , was equated to the partial molar volume of the trapped electron, which presumes that the partial molar volume of the quasi-free electron is zero. The same assumption is made here. Also the electrostriction volume for a trapped electron is assumed to be given by the classical expression.⁵ Then the volume changes observed become

TABLE 2: Results at 1 bar

liquid	temp (°C)	ΔV_{tr} (cm ³ mol ⁻¹)	V_{el} (cm ³ mol ⁻¹)	r (nm)	ΔS_{tr}^a (cal K ⁻¹ mol ⁻¹)	μ_{qf} (cm ² V ⁻¹ s ⁻¹)
1-pentene	0	-23.3	-116	0.333	-5.3	55 ± 29
	20	-27.2	-150	0.365	-5.2	
	40	-38.5	-171	0.377	-5.6	
	60	-49.0	-199	0.391	-5.7	
	80	-60.4	-237	0.415	-5.4	
cyclohexene	10	4.4	-58	0.291	1.8	174 ± 120
	20	3.7	-61	0.296	1.5	
	50	1.6	-76	0.313	0.5	
	75	-4.4	-89	0.323	-1.1	
	0	2.0	-91	0.333	0.7	
2-methyl-2-butene	20	-0.1	-107	0.349	0.0	120 ± 31
	40	-2.0	-127	0.369	-0.4	
	60	-8.8	-151	0.384	-1.3	
	80	-15.4	-181	0.404	-1.9	
	20	5.9	-80	0.324	1.6	
2,3-dimethyl-2-butene	40	3.8				96
	60	2.2				

^a Calculated from $(\alpha/\chi_T)\Delta V_{tr}$.**TABLE 3: Pressure Dependence of Trapping Volumes (cm³/mol)**

temp (°C)	pressure (bar) ^a					
	1	500	1000	1500	2000	2500
1-Pentene						
0	-23	-14	-8	-3	2	8
20	-27	-18	-10	-4	1	5
40	-38	-20	-10	-5	-2	2
60	-49	-25	-12	-6	-3	0
80	-60	-30	-14	-7	-4	-1
2-Methyl-2-butene						
20	-0.1	0.1	0.3	0.5	0.7	0.9
2,3-Dimethyl-2-butene						
20	5.9	5.0	4.2	3.3	2.5	1.6

^a 1 bar = 0.1 MPa.

$$\Delta V_1 = N \frac{e^2 \chi_T}{6\epsilon^2} (\epsilon - 1)(\epsilon + 2) + \frac{N4\pi r^3}{3} \quad (9)$$

for a cavity of radius r , where N is Avogadro's number. The first term in eq 9 is that for electrostriction, V_{el} , and the second the cavity volume, V_{cav} . The cavity radius and volume of each term are obtained by solving this equation.

The results of this analysis for the four alkenes are shown in Table 2. At 1 bar the cavity radii range from 0.29 to 0.41 nm, corresponding to cavity volumes from 90 to 170 cm³/mol. In the case of cyclohexene the electrostriction term is small because of its low compressibility, and the cavity volume dominates, leading to a positive value of ΔV_1 . The compressibility of 2,3-dimethyl-2-butene is nearly as low as that of cyclohexene, which may be the reason a positive volume change for trapping is observed. Another possibility is that the classical expression for electrostriction may not be valid for this alkene. The trap is not very deep, since the mobility is quite high and V_0 is low. Consequently, the electron wave function may be more diffuse.

As the pressure is increased, the effect of pressure on the mobility becomes smaller. Correspondingly, the magnitude of the volume change is smaller at high pressure, as shown in Table 3 for 1-pentene. This is a consequence of a decrease in χ_T . Very similar results were observed for n -pentane and n -hexane.⁴ The results for 1-pentene are unusual, however, in that at the highest pressure the mobility starts to increase, making ΔV_1 positive. In terms of the model, a decrease in the contribution of the electrostriction term is to be expected because the

compressibility decreases by more than 7-fold over the pressure range studied. The analysis, according to eq 9, indicates that the cavity radius also decreases with pressure by about 30%. The cavity radius will depend on the free energy, which is a minimum for the localized electron. Three main factors affect this energy: the free energy of cavity formation E_{cav} , the kinetic energy of the electron E_k , and the electrostatic interaction between the electron and the medium. If the cavity becomes smaller, E_{cav} and E_k increase while E_{int} decreases. The actual cavity size is determined by a detailed balance, and it is difficult to predict the effect of pressure at present. The results in Table 3 are understood in terms of a decreasing electrostriction volume and a shrinking cavity volume as the pressure increases. In 1-pentene the cavity volume dominates at very high pressure, making ΔV_1 positive at those pressures.

Entropy Changes. The entropy change associated with trapping can be expressed in a manner analogous to eq 7:

$$\Delta S_1 = \frac{-d\Delta G}{dT} = \frac{R d(T \ln K_1)}{dT} \quad (10)$$

or

$$\frac{\Delta S_1}{R} = \ln \mu_{qf} - \ln \mu - \frac{T d(\ln \mu)}{dT} \quad (11)$$

again assuming μ_{qf} is independent of temperature. Thus, eq 11 can be used to evaluate μ_{qf} if ΔS_1 of trapping is known. It has been shown that $\Delta S = (\alpha/\chi)\Delta V$ for electron attachment reactions.⁸ This relationship should also hold for trapped electrons, since the entropy change is associated with the density change around the trapped electron. In this way values of ΔS_1 were derived and the temperature dependence of the mobility was used to evaluate μ_{qf} from eq 11. The average values of μ_{qf} are shown in Table 2 and are between 55 and 174 cm² V⁻¹ s⁻¹, which is quite large compared with observed mobilities. This is consistent with the approximation made in eq 6.

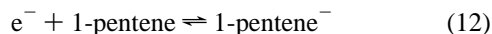
Summary

The results show that volume changes for trapping of electrons in alkenes are small and may be either positive or negative, depending on the compressibility. For n -pentane and n -hexane the trapping volumes are -28 and -22 cm³/mol at 1 bar and 25 °C.⁴ These liquids, like 1-pentene, are very compressible, which leads to large electrostriction terms.

Analysis of the results according to eq 9 leads to cavity radii of 0.35 nm for *n*-pentane and 0.32 nm for *n*-hexane. For *o*- and *m*-xylene, the values of ΔV_{tr} are 21 and 22 cm³/mol at 1 bar.² These liquids have low compressibilities, like cyclohexene, leading to smaller electrostriction terms. The same analysis as above indicates the cavity radii are 0.32 nm in these liquids. Thus, the model applies generally, with similar cavity sizes, to different classes of hydrocarbons.

The use of eq 7 to evaluate ΔV_{tr} assumes that the mobility of the quasi-free electron is independent of pressure. We also equate ΔV_{tr} with the partial molar volume of the trapped electron, which further assumes that $V(e_{qf}^-)$ is zero. This seems reasonable on the basis that the wave function of a quasi-free electron is diffuse and as such cannot electrostrict the solvent. However, a recent paper²⁹ suggests that $V(e_{qf}^-)$ is between 40 and 200 cm³/mol for certain alkanes, which would come about because of the existence of a repulsive electron–molecule potential. If this were the case here, the interpretation that the trapping volume includes both an electrostriction term and a cavity term would still apply but the cavity radius will become slightly larger to compensate; for example, if $\bar{V}(e_{qf}^-)$ were as large as +100 cm³/mol, r_{cav} would be 0.07–0.09 nm larger.

Although the two-state model applies successfully, as shown above, other interpretations of the results were considered. For example, one possibility to explain the effect of pressure on the mobility in alkenes is that electron attachment is occurring reversibly. Attachment to dialkenes^{8,9} and aromatic hydrocarbons¹¹ is known to occur and is favored at high pressure. Energetically, however, attachment to a monoalkene is unlikely. The reported electron affinity (EA) of 2-methyl-2-butene is –2.24 eV and that of 2,3-dimethyl-2-butene is –2.27 eV.³⁰ The EA of 1-pentene could be higher; we estimate about –2.0 eV.



For 300 bar and 20 °C, conditions most favorable for reaction 12, the polarization energy of the pentene anion can be estimated to be –1.5 eV, using the Born equation, and the free energy of solution of the electron would be ~0, if 1-pentene is like pentane.¹¹ Thus, the equilibrium constant for reaction 12 can be estimated to be 3×10^{-9} . Clearly, attachment is unlikely to play a role.

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