Experimental and theoretical studies of proton removal from propene

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The kinetics and energetics of proton removal from propene, which contains several sites of different acidities, were investigated both theoretically and experimentally. Rate and equilibrium constants were measured for the proton-transfer reaction $OH^- + C_3H_6 \rightleftharpoons C_3H_5^- + H_2O$ at 296 ± 2 K using the flowing afterglow technique. The rate constants were determined to be $k_{\text{forward}} = (1.1 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and $k_{\text{reverse}} = (5.4 \pm 1.9) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The ratio of rate constants, $k_f/k_r = 2.1 \pm 0.7$, was found to be in agreement with the equilibrium constant, $K = 2.2 \pm 0.8$, determined from equilibrium concentrations. *Ab initio* molecular orbital calculations predicted the removal of a methyl proton from propene to yield the allyl anion to be energetically favoured. This prediction was supported by measurements of deuteron removal from CD_3CHCH_2. The measured value of K corresponds to a standard free energy change, $\Delta G^0{}_{298}$, of -0.44 ± 0.14 kcal mol^{-1} which provided values for the standard enthalpy change $\Delta H^0{}_{298} = +0.5 \pm 0.4$ kcal mol^{-1}, the proton affinity, $PA_{298}(C_3H_5^-) = 391 \pm 1$ kcal mol^{-1}, the heat of formation, $\Delta H^0{}_{f,298}(C_3H_5^-) = 29.0 \pm 0.8$ kcal mol^{-1}, and the electron affinity $EA(CH_2CHCH_2) = 12.4 \pm 1.9$ kcal mol^{-1}. The experimentally established value for the proton affinity of the allyl anion was in reasonable accord with the value of 422.3 kcal mol^{-1} determined by calculation. The electron affinity of the allyl radical derived in this study is supported by previous calculations and several limiting values obtained experimentally.

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On a examiné, tant du point de vue théorique qu'expérimental, la cinétique et les énergies impliquées lors de l'enlèvement d'un proton du propène qui contient plusieurs sites différents par leur acidité. On a mesuré les vitesses et les constantes d'équilibre de la réaction de transfert de proton: $OH^- + C_3H_6 \rightleftharpoons C_3H_5^- + H_2O$ à 296 ± 2 K en faisant appel à la technique d'écoulement post-luminescent. On a déterminé les constantes de vitesse k_f (réaction) $= (1.1 \pm 0.3) \times 10^{-9}$ cm^3 molécule^{-1} s^{-1} et k_r (réaction inverse) $= (5.4 \pm 1.9) \times 10^{-10}$ cm^3 molécule^{-1} s^{-1}. Le rapport des constantes de vitesse $k_f/k_r = 2.1 \pm 0.7$ est en bon accord avec la constante d'équilibre de $K = 2.2 \pm 0.8$ déterminée à partir de concentrations à l'équilibre. Des calculs d'orbitales moléculaires *ab initio* ont prédit que l'enlèvement d'un proton du méthyle du propène conduisant à l'anion allyle serait favorisé d'un point de vue énergétique. Cette prédiction est appuyée par des mesures d'enlèvements de deutérons à partir du CD_3CHCH_2. La valeur mesurée de K correspond à un changement d'énergie libre standard $\Delta G^0{}_{298}$ de -0.44 ± 0.14 kcal mol^{-1} qui fournit des valeurs de changement d'enthalpie standard $\Delta H^0{}_{298} = +0.5 \pm 0.4$ kcal mol^{-1}, d'affinité de proton $PA_{298}(C_3H_5^-) = 391 \pm 1$ kcal mol^{-1}, de chaleur de formation $\Delta H^0{}_{f,298}(C_3H_5^-) = 29.0 \pm 0.8$ kcal mol^{-1}, et d'affinité électronique $EA(CH_2CHCH_2) = 12.4 \pm 1.9$ kcal mol^{-1}. L'accord entre la valeur établie expérimentalement pour l'affinité du proton de l'anion allylique avec la valeur de 422.3 kcal mol^{-1} déterminée à partir de calculs est raisonnable. L'affinité pour un électron du radical allyle obtenue dans cette étude est en accord avec des calculs antérieurs et plusieurs valeurs limitantes obtenues expérimentalement.

[Traduit par le journal]

Introduction

Gas-phase measurements of rate and equilibrium constants for proton-transfer reactions of the type

$$[1] \qquad X^- + YH \rightleftarrows Y^- + XH$$

constitute an important means of determining intrinsic thermochemical properties for Brønsted acids and their conjugate bases (1–5). In particular, such measurements have provided proton affinities and heats of formation of anions and electron affinities of their corresponding radicals of sufficient accuracy to be of both academic and practical value. When the proton donor, YH, has only one acidic site the structure of the anion, Y^-, is likely to be unique so that the corresponding measurements and thermodynamic assignments should be unambiguous. For proton donors with more than one acidic site, YH_n ($n > 1$), several tautomeric forms of the conjugate base, YH^-_{n-1}, having different energies, may become both thermodynamically and kinetically acces-

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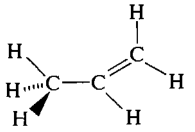
sible although the higher energy forms will be discriminated against as the reaction exothermicity decreases.

This study is directed towards the determination of the proton affinity, PA, and heat of formation, $\Delta H^0{}_f$, of the allyl anion, and the electron affinity, EA, of the allyl radical. The allyl anion was derived from propene by proton removal according to the reaction:

$$[2] \qquad OH^- + CH_3CHCH_2 \rightarrow \overline{CH_2\overset{-}{C}HCH_2} + H_2O$$

In its optimum conformation propene has been shown (6, 7) to have one hydrogen of the methyl group in the plane of the carbon nuclei as shown in structure **1**. The rationale for this eclipsed structure being preferred is that this configuration maximizes the distance between the out-of-plane hydrogen atoms and the double bond, thereby decreasing the destabilizing 4π-electron interaction. In this conformation the propene molecule has five chemically different protons and deprotonation could therefore conceivably produce five different anions. Reaction 2, which was chosen deliberately for its low exothermicity (2), should be selective in establishing the allyl anion which is expected to be the lowest energy tautomer. This was confirmed by *ab initio* molecular orbital calculations. An attempt was also made to establish experimentally additional confidence in the assignment of the allylic structure to the carbanion by measurements of the reaction of OH^- with propene-3,3,3-d_3 designed to identify the most acidic site on propene.



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Experimental

The experiments were carried out in a flowing plasma-mass spectrometer (flowing afterglow) system for which the details of construction and the method of operation and data analysis have been described elsewhere (8). Hydrogen and helium were both used as the carrier gas. The OH^- ions were produced either via proton transfer from H_2O to NH_2^- or to H^- according to the rapid reactions (9)

$$[3] \qquad NH_2^- + H_2O \rightarrow OH^- + NH_3$$

$$[4] \qquad H^- + H_2O \rightarrow OH^- + H_2$$

or by electron impact on water vapour added upstream from the ionizer (10). NH_2^- and H^- were generated by dissociative ionization of NH_3 introduced upstream of the electron gun. When helium was used as the carrier gas small amounts of H_2 were added to remove the O^- (also produced by electron impact of H_2O) according to the associative detachment reaction (11):

$$[5] \qquad O^- + H_2 \rightarrow H_2O + e$$

In these experiments the filament of the electron gun was biased negatively in the range from 35 to 70 V with respect to the grid envelope held at ground potential. The emission current was typically 1 mA. The water vapour, which also served as the neutral back reactant, was introduced through a capillary tube in the usual manner either in its pure form at pressures below its vapour pressure, or diluted with helium (1 part H_2O to 9 parts He). The mixtures were prepared by allowing the H_2O vapour to equilibrate in the gas inlet system to the ambient temperature (at a pressure <0.8 of the vapour pressure) and subsequently adding helium. Measurement of the H_2O flow required a separate determination of the viscosity of both the pure and diluted vapour (4). The propene was added sufficiently downstream of the ion production region to ensure that all the reactions producing OH^- had gone to completion and that the OH^- ions experienced enough collisions with the carrier gas to become thermalized at the ambient temperature (296 ± 2 K). The ions present in the flowing plasma were sampled through a small orifice in the tip of a nose cone situated at the end of the reaction region and mass analyzed with a quadrupole mass filter. The variation in the reactant and product ion signals as a function of neutral reagent addition provided the raw data from which the rate and equilibrium constants were determined (8).

A number of tests were carried out to establish confidence in the attainment of true equilibrium. The forward and reverse rate constants and the ratio of the ion concentrations were determined at different relaxation and reaction times, various flows of neutral back reactant, in both helium and hydrogen at several pressures, at various electron and ion densities, and under different sampling conditions.

The gases used were helium (Linde, Prepurified Grade, 99.995% He), hydrogen (Linde, Very Dry Grade, 99.95% H_2), ammonia (Matheson, anhydrous, $>99.99\%$ NH_3 (liquid phase)), propene (Matheson, C.P. Grade 99.0% C_3H_6 (liquid phase)), and propene-3,3,3-d_3 (Merck, Sharp & Dohme, $>98\%$ D). The water vapour was derived from either boiled tap water or boiled distilled water.

Results

Experimental

Figure 1 shows the data obtained upon the addition of C_3H_6 into a He–H_2O plasma in which OH^- is initially a dominant negative ion. The negative ions with $m/e = 17, 35, 37, 41$, and 46, the major ions present in the range $m/e = 1$–60 for the range of C_3H_6 flows used, were monitored as a function of C_3H_6 addition. These ions were identified as OH^-, Cl^- ($m/e = 35$ and 37), $C_3H_5^-$, and NO_2^- respectively. Cl^- and NO_2^-, which are unreactive impurity ions generally present in the negative ion spectrum, were monitored to confirm constant sampling throughout an experiment. The behaviour shown is representative of the observations made in 12 separate experiments performed under the following conditions: effective reaction length, $L = 61$ cm (in 7 experiments) and 85 cm (in 5 experiments), average flow velocity, $\bar{v} = 7.7$ to 8.1×10^3 cm s^{-1}, total pressure, $P = 0.390$ to 0.76 Torr, and flow of $H_2O = 7.9 \times 10^{16}$ to 3.47×10^{18} molecules s^{-1}.

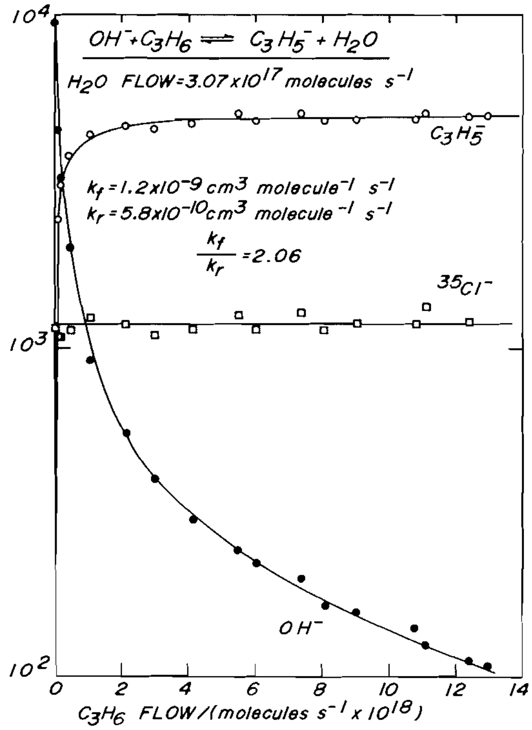


FIG. 1. The variation of the major negative ion signals recorded upon the addition of C_3H_6 into a flowing H_2O–He plasma in which OH^- is initially a dominant negative ion. The solid line through the OH^- decay is a computer fit. $T = 296$ K, $P = 0.54$ Torr, $\bar{v} = 8.1 \times 10^3$ cm s^{-1}, and $L = 61$ cm.

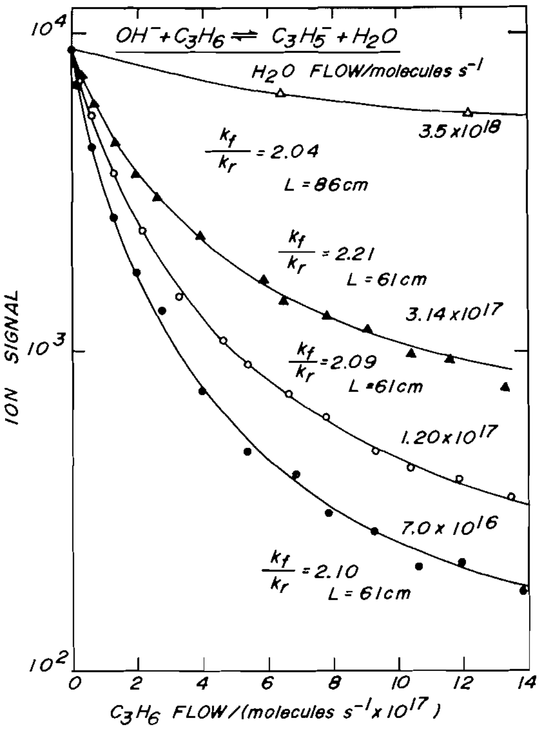


FIG. 2. The variation of the OH^- signals as a function of C_3H_6 addition at various additions of H_2O. $P = 0.54$ Torr, $T = 296$ K, and $\bar{v} = 7.7$–8.1×10^3 cm s^{-1}. The points are experimental and the solid lines are computer fits.

Addition of C_3H_6 gave rise to the rapid decline of the OH^- signal and the concomitant increase in the $C_3H_5^-$ signal. There was no evidence for the occurrence of competing reactions so that the entire variation in the OH^- and $C_3H_5^-$ signals with C_3H_6 addition could be ascribed to the transfer of a proton. The curvature in the logarithmic decay of the OH^- signal can be attributed to the occurrence of the reverse proton transfer from H_2O to $C_3H_5^-$. The solid curve drawn through the data points for the OH^- decay represents the best computer fit obtained using analysis B of ref. 8.

In eight investigations the amount of back-reaction was sufficient to introduce curvature in the OH^- decay without attaining equilibrium at low C_3H_6 flows. This allowed the determination of unique values for $k_f = (1.1 \pm 0.1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, for $k_r = (5.4 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and for $(k_f/k_r)_{ne} = 2.1 \pm 0.3$. In three other investigations the reaction was already so close to equilibrium at low C_3H_6 flows that the application of the fitting procedure could only yield a unique value for the ratio of rate constants, $(k_f/k_r)_e = 2.1 \pm 0.1$. Figure 2 shows a family of OH^- decays which encompass the range of back-reactant H_2O flows as well as the two values of the reaction length employed in this study.

In all 12 experiments equilibrium was established at high flows of C_3H_6 and fits to the linear portions of the ratio plots (analysis C in ref. 8) allowed the determination of the equilibrium constant, K, from the equilibrium concentrations. The ratio of the ion signals, $I(C_3H_5^-)/I(OH^-)$, when corrected for mass discrimination, is a measure of the ratio of the ion concentrations $[C_3H_5^-]/[OH^-]$. The method employed for the determination of the mass discrimination factor, m, has been reported previously (8). Figure 3 indicates the approach to and attainment of equilibrium at several flows of back-reactant H_2O. At the highest flow of H_2O equilibrium is established at the lowest measurable addition of C_3H_6. The 12 measurements led to a mean value for K of 2.2 ± 0.1.

The sampling conditions were altered in several of the 12 experiments either by varying the potential of the nose cone with respect to the flow tube (NP) at a fixed potential difference between the nose cone and the axis of the quadrupole mass filter (AP) or by adjusting AP at a fixed value for NP. Both k_f/k_r and K were observed to be independent of these variations within the experimental uncertainty.

Our analysis of the approach to and attainment

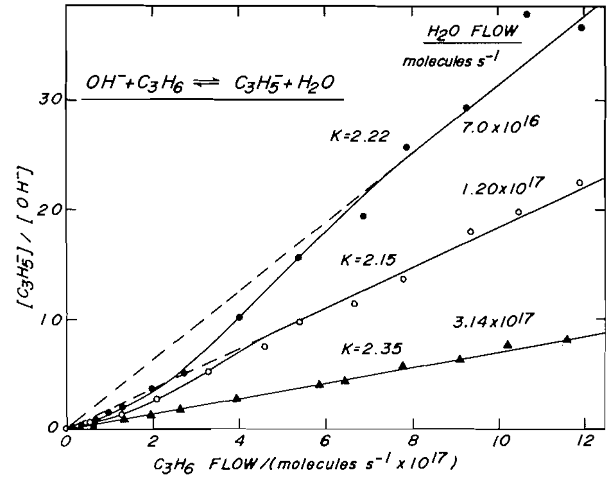


FIG. 3. The variation of $[C_3H_5^-]/[OH^-]$ as a function of C_3H_6 flow at various additions of H_2O. The slopes of the straight lines through the experimental points are proportional to the equilibrium constant K. $L = 61$ cm, $P = 0.54$ Torr, $T = 296$ K, and $\bar{v} = 8.1 \times 10^3$ cm s^{-1}. $m = 2.11$, 2.98, and 2.35 respectively from high to low H_2O flow.

of equilibrium in the flowing afterglow assumes equal diffusive losses for the reactant and product ions (8). Under normal operating conditions the loss of negative ions due to diffusion in the flowing plasma is controlled by positive ion–electron ambipolar diffusion. In these experiments H_3O^+ ($m/e = 19$) was the dominant positive ion present in the H_2O–He(H_2) plasma. As C_3H_6 was added to the reaction region the H_3O^+ was observed to react rapidly via proton transfer to give $C_3H_7^+$ ($m/e = 43$) as the dominant positive ion with $k = (1.5 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. For positive ions with $m/e > 20$ the ion–electron ambipolar diffusion coefficients in hydrogen and helium are very similar (12). Therefore, the assumption of equal losses for OH^- and $C_3H_5^-$ by diffusion should not represent a serious error. It is possible to test the validity of this assumption experimentally by adding trace amounts of SF_6 into the reaction region (13). The addition of SF_6 changes the diffusion mode from positive ion – electron to positive ion – negative ion which is less rapid and less discriminating.

Figures 4 and 5 explore the effect of diffusion on the equilibrium constant measurements. Figure 4 shows the expected enhancement of the ion signals as SF_6 is added. However, the shape of the OH^- decay and hence the value of k_f/k_r derived from a fit to this decay remains essentially unchanged as would be expected if OH^- and $C_3H_5^-$ have similar diffusion coefficients. The equilibrium constants derived from the ion-signal ratio at equilibrium in the absence and presence of SF_6 again agree within experimental error when a correction is made for mass discrimination (Fig. 5).

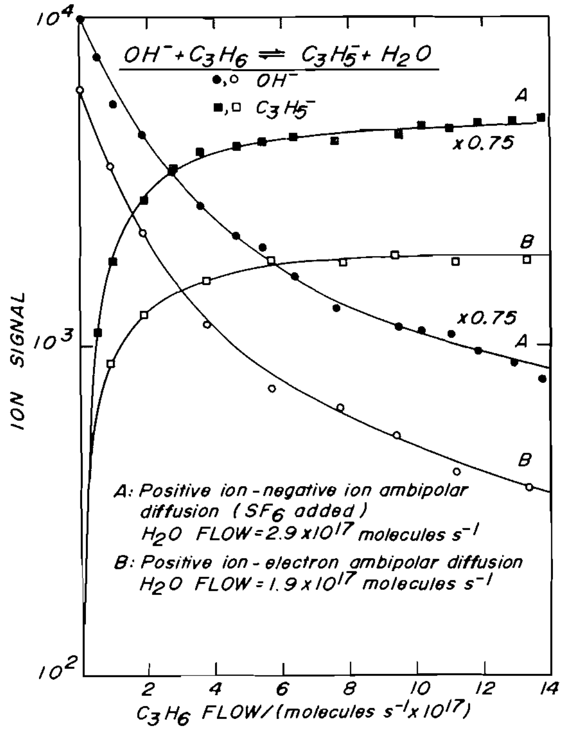


FIG. 4. The effect of SF_6 addition on the variation of the OH^- and $C_3H_5^-$ signals with C_3H_6 addition. The experimental operating conditions were otherwise quite similar. The curves drawn through the OH^- decays represent best computer fits to the experimental points: curve A, $k_f/k_r = 2.3$; curve B, $k_f/k_r = 2.1$. $P = 0.53$ Torr, $\bar{v} = 8.1 \times 10^3$ cm s^{-1}, $T = 296$ K, and $L = 61$ cm.

Table 1 summarizes the experimental results and includes an assessment of the accuracy in each case. The sources of error have been described previously (8, 13). In these experiments the largest uncertainty in the determination of k_f/k_r and K was introduced by the uncertainty in the measurement of the flow of water vapour.

Figure 6 shows the observed variation in the major negative ion signals detected upon the addition of propene-3,3,3-d_3 into a He–H_2O plasma in which OH^- was initially a dominant negative ion. The introduction of CD_3CHCH_2 into the reaction region gave rise to a decrease in the OH^- signal and a concomitant increase in the ion signals at $m/e = 18$ (OD^-), $m/e = 41$ ($C_3H_5^-$), $m/e = 42$ ($C_3DH_4^-$), $m/e = 43$ ($C_3D_2H_3^-$), and $m/e = 44$ ($C_3D_3H_2^-$). There was no evidence for subsequent rapid reaction of any of the carbanions with CD_3CHCH_2.

Theoretical

The possible anions derived from the abstraction

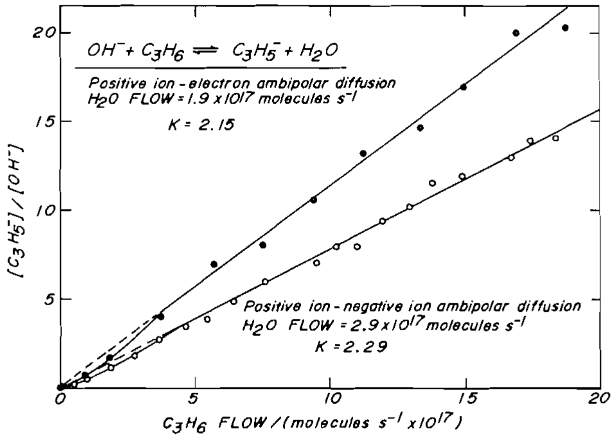


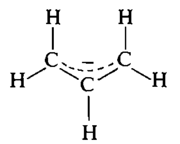
FIG. 5. The effect of SF_6 addition on the variation of ion ratio $[C_3H_5^-]/[OH^-]$ as a function of C_3H_6 addition. L = 61 cm, P = 0.54 Torr, $\bar{v} = 8.1 \times 10^3$ cm s^{-1}, T = 296 K, and m = 2.98 (without SF_6) and 1.84 (with SF_6 added).

TABLE 1. Experimental results for the reaction $OH^- + C_3H_6 \rightleftharpoons C_3H_5^- + H_2O$ at 296 ± 2 K

	Number of measurements	Results and precision	Accuracy (%)
k_f	8	$(1.1 \pm 0.1) \times 10^{-9a}$	±30
k_r	8	$(5.4 \pm 1.0) \times 10^{-10a}$	±35
$(k_f/k_r)_{nc}$	8	2.1 ± 0.3	±30
$(k_f/k_r)_c$	3	2.1 ± 0.1	±30
K	12	2.2 ± 0.1	±35

[a] Units of cm^3 $molecule^{-1}$ s^{-1}.

of the five chemically different protons of propene were examined using *ab initio* molecular orbital calculations. The removal of any proton from the methyl group was found to produce the same *planar* allyl anion. This reduces the number of possible anions to four (structures **2** to **5**). The cyclopropyl anion, another possible tautomer, was not examined in this study. It cannot be established directly by proton removal from propene and, furthermore, earlier calculations have established it to be very unstable (14).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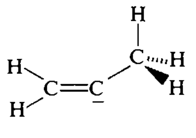
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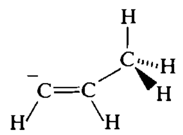
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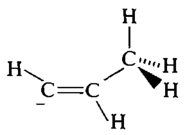
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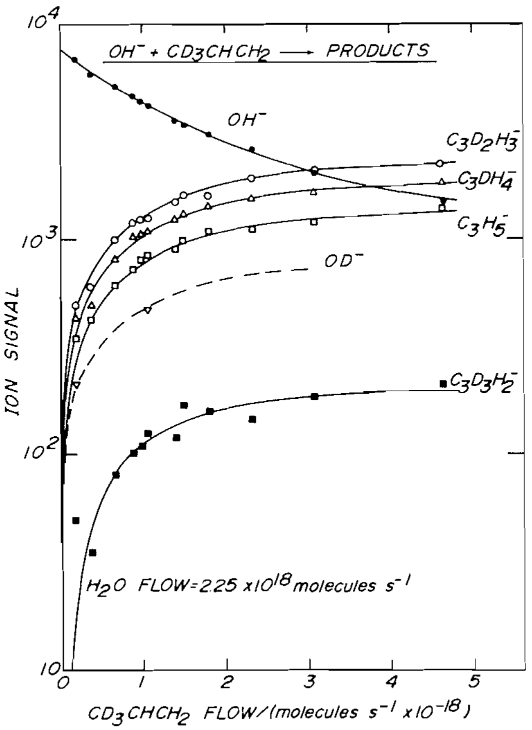


FIG. 6. Observed variation of major negative ion signals recorded upon the addition of propene-3,3,3-d_3 into a flow H_2O-He plasma in which OH^- is initially a dominant negative ion. The product ion signals have not been corrected for mass discrimination. T = 296 K, P = 0.357 Torr, $v = 7.8 \times 10^3$ cm s^{-1}, and L = 59 cm.

The geometry of propene has been optimized with the minimal STO-3G basis set (15) and there is good agreement between the experimental (16) and computed (6) geometries. This same basis set was employed to optimize the geometries of the four anions. Larger basis set (6-31G) calculations (17) using these optimum geometries were then performed to obtain more reliable energies for these anions.

Removal of a proton from the methyl group produces the planar allyl anion (**2**) in which both terminal methylene groups are equivalent. In this structure (Fig. 7) the carbon–carbon bond lengths (1.370 Å) are intermediate between single and double bond lengths and are close to previously calculated values of 1.38 Å (14) and 1.388 Å (18). The internal angle between the carbon atoms (132.9°) is almost 8° larger than in propene, a fact which is attributable to the negative charge formally located on the terminal carbon atoms. Again there is good agreement with the literature values of 133.1° (18) and 134° (19).

Preliminary studies on the other three anions showed the methyl group to prefer the same conformation as in propene. In the subsequent geometry

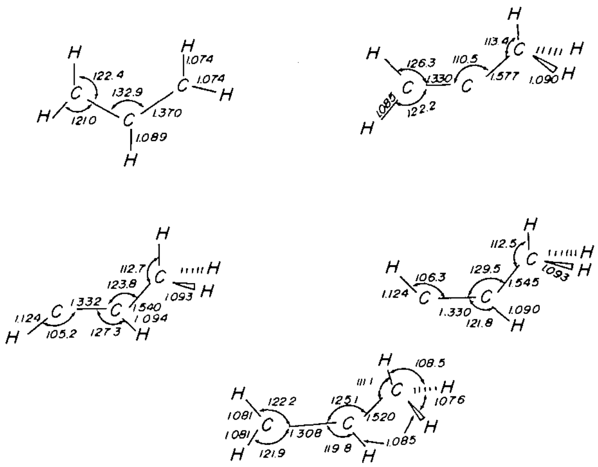


FIG. 7. Optimum geometries of propene and the tautomeric forms of $C_3H_5^-$ as computed with the STO-3G basis set. Bond lengths are given in angstroms and angles in degrees.

optimizations it was assumed that the bond lengths and angles for all three hydrogens in a methyl group were the same. This approximation reduced the number of geometric parameters and thereby reduced the computational cost of the optimizations. An estimate of the magnitude of the error introduced by this approximation is available from the same type of optimization on propene. The overall geometry computed for propene using this approximation is almost identical to that produced in the *complete* optimization and the total energy is inferior by only 0.5 kcal/mol (at STO-3G level) and by less than 0.13 kcal/mol with the more extensive 6-31G basis set.

Geometry optimizations on anions **3**, **4**, and **5** produced bond lengths similar to, but slightly longer than, the corresponding bonds in propene, showing the valence bond structures to be satisfactory descriptions of the molecular structure. The angle between the three carbon atoms appears to be particularly sensitive to the site of deprotonation. Removal of the proton from the central carbon atom produces a decrease in this angle by almost 15°, possibly caused by the newly generated σ-lone pair repelling the two bonds. Deprotonation of the methylene group produces less dramatic changes and these can also be attributed to lone pair – bond pair repulsions. Comparison of the relative energies of the carbanions as computed by both the STO-3G and 6-31G basis sets shows the allyl anion (**2**) to be the most stable by a substantial margin (Table 2 and Fig. 8).

Table 2 also includes proton removal energies taken as the difference in the computed energies of C_3H_6 and $C_3H_5^-$ for the reaction

$$[6] \qquad C_3H_6 \rightarrow C_3H_5^- + H^+$$

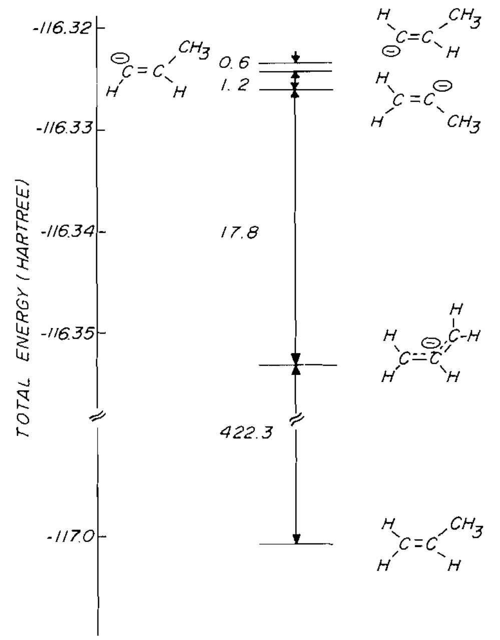
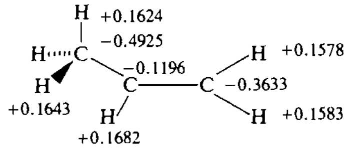


FIG. 8. Relative energies of propene and the tautomeric forms of $C_3H_5^-$ as computed with the 6-31G basis set. Energy differences are in kcal mol^{-1}.

Since these proton removal energies may also be regarded as acidities, the order of acidities as computed by both the STO-3G and 6-31G basis sets is $CH_3 \gg CH > CH_2$. This order, deduced from the equilibrium energies, differs from that predicted by the computed net-atomic charges from a Mulliken overlap population on propene (using the 6-31G basis

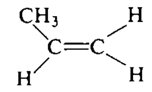
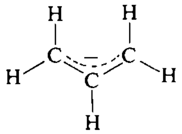
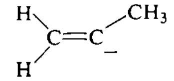
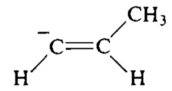
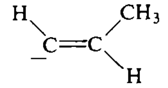


set), showing use of a ground state property is unsatisfactory to predict equilibrium stabilities.

Discussion

Flowing afterglow studies of the reaction of OH^- with propene have been performed previously by Bohme *et al.* (2) who reported a value for $k_f = 2.7 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and by Bierbaum *et al.* (20) who determined a value for $k_f = 2.5 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The observations reported here, which provided a value for $k_f = 1.1 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, suggest that these earlier numbers should be regarded as lower limits to the true value of k_f. Our experience indicates that only small amounts of H_2O are needed to achieve equilibrium for this reaction under typical flowing afterglow operating conditions even at low propene additions. Indeed we have observed that impurity amounts of

TABLE 2. Computed total energies and proton removal energies

Species	Total energy (hartree)		Proton removal energy[a] (kcal mol^{-1})	
	STO-3G	6-31G	STO-3G	6-31G
	−115.66030[b]	−117.02768[b]		
	−114.83832	−116.35495	516.0	422.3
	−114.82613	−116.32655	523.6	440.1
	−114.82164	−116.32468	526.4	441.3
	−114.82225	−116.32368	526.1	441.9

[a] Not corrected for zero-point energy or thermal energy.
[b] Reference 6.

H_2O can result in sufficient back-reaction to modify the OH^- decay to such an extent that the application of the standard rate constant analysis can only provide a lower limit to the true value of the forward rate constant (8).

The results given in Table 1 indicate that satisfactory agreement is found in this study between the following quantities: (*1*) the ratio of rate constants, $(k_f/k_r)_{ne}$, determined from the fit to the OH^- ion decays obtained under nonequilibrium conditions; (*2*) the ratio of rate constants, $(k_f/k_r)_e$, determined from the fit to the OH^- ion decays under equilibrium conditions; and (*3*) the equilibrium constant, K, determined from equilibrium concentrations. It should be emphasized here that $(k_f/k_r)_{ne}$ and $(k_f/k_r)_e$ do not require the correction for mass discrimination necessary in the determination of K from the equilibrium concentrations. These results, together with the observed independence of the measured ratio of rate constants and the equilibrium constant on the range of reaction times, neutral concentrations, electron and ion densities (diffusion mode), and the potentials in the sampling region, provide confidence that these measured values represent a true equilibrium constant.

The values of k_f/k_r and K provide a best estimate (21) of the true value (a weighted mean) of the equilibrium constant at 296 ± 2 K of 2.1 with a standard error of ±0.5. The thermodynamic information which can be derived from a knowledge of this equilibrium constant is summarized in Table 3. The value of $K = 2.1 \pm 0.5$ corresponds to a standard free energy change, $\Delta G^0{}_{298}$, of -0.44 ± 0.14 kcal mol^{-1}. A standard entropy change, $\Delta S^0{}_{298}$, of 3 ± 1 eu may be calculated from the reported values of the standard entropies of H_2O, C_3H_6, and OH^- (22, 23) and an estimated value for $S^0{}_{298}$ ($C_3H_5^-$) of 63 ± 1 cal deg^{-1} mol^{-1}. This leads to a standard enthalpy change, $\Delta H^0{}_{298}$, of $+0.5 \pm 0.4$ kcal mol^{-1}.

The standard enthalpy change determined in this study corresponds to a difference in proton affinity $PA(C_3H_5^-) - PA(OH^-) = +0.5 \pm 0.4$ kcal mol^{-1}. Adoption of the values for $\Delta H^0{}_{f,298}$ (H_2O, OH, H^+) given in the JANAF tables (22) and $EA_0(OH) = 42.09 \pm 0.043$ kcal mol^{-1} (24) leads to a value for $PA_{298}(OH^-) = 390.9 \pm 0.09$ kcal mol^{-1} and thus a value for $PA_{298}(C_3H_5^-) = 391.4 \pm 0.5$ kcal

TABLE 3. Thermodynamic parameters for the reaction $OH^- + C_3H_6 \rightleftharpoons C_3H_5^- + H_2O$ at 296 ± 2 K. The standard error is given along with the best estimate of the true value

$K = 2.1 \pm 0.5$
$\Delta G^0 = -0.44 \pm 0.14$ kcal mol^{-1}
$\Delta S^0 = +3 \pm 1$ cal deg^{-1} mol^{-1} (estimated)
$\Delta H^0 = +0.5 \pm 0.4$ kcal mol^{-1}

mol^{-1}. However, the equilibrium measurements per se do not unequivocably establish the tautomeric form of $C_3H_5^-$. Although it is reasonable to expect that the equilibrium involves the allyl anion which our calculations have shown to be the most stable form, the possibility remains that the reaction of OH^- with propene produces a higher energy tautomer which does not isomerize in the helium or hydrogen bath to the allylic form prior to reverse reaction with H_2O. In this case the proton affinity determined from these measurements would refer to the higher energy form and not to the allyl anion. However, this possibility can be readily discounted by a comparison of the ~18 kcal mol^{-1} difference between the allyl anion and the next lowest energy tautomer established by our calculations and the difference allowed by experimental observations. A proton affinity of 391 kcal mol^{-1} for the high energy tautomer would require a proton affinity for the allyl anion of only 373 kcal mol^{-1}. Such a low value would make the allyl anion thermodynamically accessible to the reaction

$$[7] \qquad CH_3O^- + C_3H_6 \rightleftharpoons C_3H_5^- + CH_3OH$$

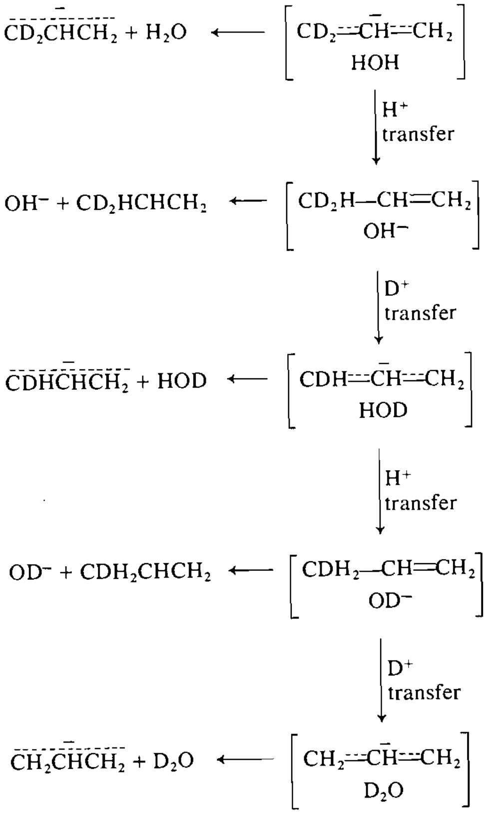
since $PA_{298}(CH_3O^-) = 381 \pm 2$ kcal mol^{-1} (25). However, equilibrium measurements made in this laboratory indicate a value for $K_7 < 10^{-5}$ which requires the proton affinity for the allyl anion to be >388 kcal mol^{-1} and, when combined with the value for $PA_{298}(C_3H_5^-) = 391$ kcal mol^{-1}, would allow a proton affinity difference of at most 3 kcal mol^{-1} between the allyl ion and the next lowest energy tautomer. This result is clearly not supported by the theoretical expectations. On this basis we conclude that the carbanion produced by the reaction of OH^- with propene is indeed the allyl anion.

Our assignment of the allylic structure to the observed $C_3H_5^-$ is also supported, albeit indirectly, by the deuterated propene experiments whose results were considerably more complex than we had naively anticipated. Although the expected $C_3D_2H_3^-$ was the dominant product ion, significant concentrations of other carbanions with various extents of deuteration, viz. $C_3DH_4^-$, $C_3H_5^-$, and $C_3D_3H_2^-$, as well as some OD^- were observed. The $C_3H_5^-$, which cannot arise from the reaction of OH^- with CD_3CHCH_2, is presumed to result from secondary hydrogen–deuterium exchange reactions of the various deuterated carbanions with water vapour (the parent gas of OH^-) present in the reaction region according to

$$[8] \qquad \begin{aligned} C_3D_2H_3^- + H_2O &\rightarrow C_2DH_4^- + HOD \\ &\rightarrow C_3H_5^- + D_2O \end{aligned}$$

$$[9] \qquad C_3DH_4^- + H_2O \rightarrow C_3H_5^- + HOD$$

The exchange is believed to proceed in the reaction intermediate via sequential proton–deuteron transfer made possible by the symmetry of the allylic structure (Scheme 1). This sequence, which is meant only to be illustrative of the general nature of the mechanism, does not include all modes of proton–deuteron transfer. An analogous mechanism should also be involved for the forward reaction (Scheme 2). This reaction sequence (again abridged) allows the formation of $C_3D_3H_2^-$ in addition to the other anions observed.[2]



SCHEME 1

The thermochemical values for the allyl anion and radical derived from the equilibrium constant measurement for reaction 2 are summarized in Table 4. A value for $\Delta H^0{}_{f,298}$ (allyl anion) of 29.0 ± 0.8 kcal mol^{-1} is obtained when the values for $\Delta H^0{}_{f,298}(OH^-) = -34.3 \pm 0.4$ (22, 24), $\Delta H^0{}_{f,298}(H_2O) = 57.7979$ kcal mol^{-1} (22), $\Delta H^0{}_{f,298}(C_3H_6) = 4.88 \pm 0.1$ kcal mol^{-1} (23), and the present value of $\Delta H^0{}_{298}$ for reaction 2 are combined according to

$$[10] \qquad \Delta H^0{}_f(\overline{CH_2\overset{-}{C}HCH_2}) = \Delta H^0{}_f(C_3H_6) - \Delta H^0{}_f(H_2O) + \Delta H^0{}_f(OH^-) + \Delta H^0$$

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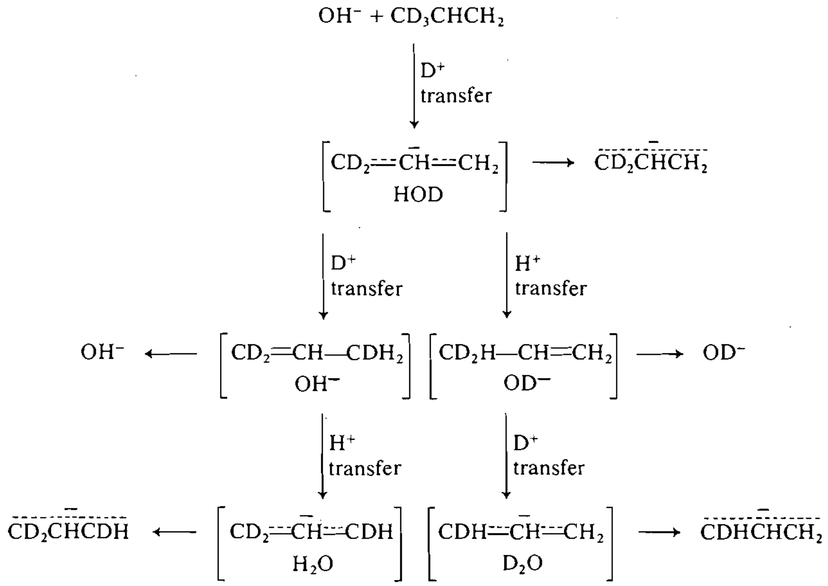
[2] J. H. Stewart, R. H. Shapiro, C. H. DePuy, and V. M. Bierbaum have independently proposed a similar mechanism of sequential proton–deuteron transfer in connection with their flowing afterglow studies of reactions of carbanions with D_2O (C. H. DePuy, private communication).



SCHEME 2

TABLE 4. Thermochemical values determined in this study

$\mathrm{PA_{298}}(\overline{\mathrm{CH_2}}\overline{\overline{\mathrm{CH}}}\overline{\mathrm{CH_2}}) = 391.4 \pm 0.5$ kcal mol^{-1}

$\Delta H^0{}_{\mathrm{f,298}}(\overline{\mathrm{CH_2}}\overline{\overline{\mathrm{CH}}}\overline{\mathrm{CH_2}}) = 29.0 \pm 0.8$ kcal mol^{-1}

$\mathrm{EA_{298}(CH_2CHCH_2)} = 12.4 \pm 1.9$ kcal mol^{-1}

Combination of this result for the heat of formation of the allyl anion with a value of 41.4 ± 1 kcal mol^{-1} for the heat of formation of the allyl radical (26) according to

$$\mathrm{EA(CH_2CHCH_2)} = \Delta H^0{}_{\mathrm{f}}(\mathrm{CH_2CHCH_2}) - \Delta H^0{}_{\mathrm{f}}(\overline{\mathrm{CH_2}}\overline{\overline{\mathrm{CH}}}\overline{\mathrm{CH_2}})$$

leads to a value for $\mathrm{EA_{298}(CH_2CHCH_2)} = 12.4 \pm 1.9$ kcal mol^{-1}.

Our experimental value for $\mathrm{PA_{298}}$(allyl anion) = 391.4 ± 0.5 kcal mol^{-1} is somewhat (~8%) lower than the absolute value (not corrected for zero-point energy or thermal energy) of 422.3 kcal mol^{-1} derived from our molecular orbital calculations with the 6-31G basis set. Such a difference between theory and experiment is not unexpected (4) and could be reduced with the use of a more extensive basis set. Other theoretical studies have provided a variety of values for the electron affinity of the allyl radical. An early molecular orbital calculation by Hush and Pople (27) provided a value for $\mathrm{EA(CH_2CHCH_2)} = 5.5$ kcal mol^{-1}. Subsequent calculations by Ehrenson (28) and Hoyland and Goodman (29) led to values of −3.2 and 12 kcal mol^{-1}, respectively. Reliable experimental values were not available for comparison at that time. More recently, flowing afterglow measurements have provided an upper limit for $\mathrm{EA_{298}(CH_2CHCH_2)} \leq 12.6 \pm 0.8$ kcal mol^{-1} (corrected for entropy changes), based on the observation of the electron transfer reaction

$$[11] \qquad \overline{\mathrm{CH_2}}\overline{\overline{\mathrm{CH}}}\overline{\mathrm{CH_2}} + \mathrm{O_2} \rightarrow \mathrm{O_2}^- + \mathrm{CH_2CHCH_2}$$

with $k_{11} = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (28). The electron affinity of $\mathrm{O_2}$ at 298 K is 11.6 kcal mol^{-1} (30) and we have allowed for a possible endoergicity of 0.5 kcal mol^{-1} given by $-RT \ln k_{11}/k_{\mathrm{L}}$, where k_{L} is the Langevin collision rate constant (31). A lower limit for $\mathrm{EA_{298}(CH_2CHCH_2)}$ of 12.1 ± 1.8 kcal mol^{-1} (corrected for entropy changes) can be derived (2) from the observation of reaction 2. These limiting values and the value calculated most recently by Hoyland and Goodman (29) are in accord with the value of 12.4 ± 1.9 kcal mol^{-1} determined in the present study. Very recently Zimmerman and Brauman (32) have reported electron photodetachment measurements for $\overline{\mathrm{CH_2}}\overline{\overline{\mathrm{CH}}}\overline{\mathrm{CH_2}}$ produced by reaction 2. A theoretical fit to the relative cross-sections near threshold provided a value for the electron affinity at 0 K of 12.7 ± 1.2 kcal mol^{-1} where the error limits reflect the lack of data at threshold.

Acknowledgements

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