Reactions of O^- with Various Alkanes: Competition between Hydrogen Abstraction and Reactive Detachment

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We have studied the rate constants and product branching percentages of the reactions of O^- with a large number of alkanes: ethane, propane, butane, isobutane (2-methylpropane), pentane, isopentane (2-methylbutane), neopentane (2,2-dimethylpropane), hexane, heptane, octane, isooctane (2,2,4-trimethylpentane), decane, and dodecane. The efficiencies for the reactions of O^- with ethane, propane, and butane increase with increasing size, becoming collisional for butane at room temperature. A small temperature dependence is found. For pentane and larger alkanes, the reactions are collisional at all temperatures, within our uncertainty. In contrast to a previous study, there are two significant reaction channels observed: a hydrogen abstraction channel yielding OH^- and a reactive detachment channel yielding neutral products and a free electron. In the normal alkane series, the fraction of OH^- produced decreases exponentially with increasing polarizability, i.e., alkane size. Isobutane and isopentane react similarly to their normal alkane counterparts, while isooctane and neopentane produce significantly more OH^- than octane and pentane, respectively. Taken together, the branching fraction results indicate that the reactive detachment channel is due to abstraction of two hydrogen atoms from adjacent carbons within the alkane.

Introduction

The rich and interesting chemistry of the atomic oxygen anion, O^-, has been the focus of numerous kinetics studies; the reader is referred to an excellent review by Lee and Grabowski[1] which summarizes the chemistry of this important ion. One of the more intriguing aspects of O^- chemistry is that the ion has the ability to abstract an H_2^+ from many organic species, including alkenes and alkynes.[1] This stems from the fact that the atomic oxygen anion has a large hydrogen atom affinity which allows for hydrogen atom abstraction from many compounds. Also, the resulting OH^- product ion is a strong base, allowing for H^+ transfer from many of the products of the initial hydrogen abstraction. This interesting characteristic of O^- chemistry has often been utilized in the synthesis of unusual organic anions.

The chemistry of O^- with alkanes, on the other hand, has been viewed as rather unexciting, as all reactions have been believed to proceed exclusively through hydrogen atom abstraction.[2] For example, the reaction of O^- with methane, which has recently been studied in detail,[3,4] is rather inefficient and proceeds via hydrogen atom transfer. (Interestingly, the reaction does reveal a large isotope effect and dependence on the CH_4 stretching vibrations.) To our knowledge only one study of the larger (noncyclic) alkanes has been reported. In 1969, Bohme and Fehsenfeld[2] found that O^- reacts with ethane, propane, and butane at roughly half the collision rate and proceeds exclusively by hydrogen atom transfer. The simplicity of these results indicated that further study on even larger alkanes would produce little additional information on the reactivity.

We have undertaken an extensive study of the reactions of primary atmospheric ions with the larger alkanes commonly found in fuels such as gasoline or kerosene in order to explore the possibility that such reactions could enhance the rate of combustion or ignition.[5] Because ion−molecule reactions are typically 100 times faster than conventional combustion reactions, i.e., those between neutral species, they may affect the rate of combustion or ignition by breaking chemical bonds, creating radicals, and speeding up the first and slowest step in the combustion reaction. In the course of this survey, we examined the reactivity of O^- with several larger alkanes. We found that the rate constants for these reactions were large, as would be indicated by the previous work on alkanes. However, we found that the reactions did not proceed exclusively by hydrogen abstraction. In fact, we found that the majority of the reactivity was due to reactive detachment (production of electrons as the charge carrier).

In this paper, we report the rate constants and product branching percentages for the reactions of O^- with most normal alkanes from C_2 to C_{12}, as well as four branched alkanes and one completely deuterated compound, C_3D_8. The reactions of O^- with ethane and propane were studied at 178, 300, and 500 K, while all other alkane reactions were studied at 300 and 500 K.

Experimental Section

The measurements were made using the Air Force Research Laboratory variable temperature-selected ion flow tube.[6] Instruments of this type have been the subject of review,[7] and only those aspects relevant to the present study will be discussed in detail. The reactant ions were produced in a moderate pressure ion source (0.1−1 Torr) by electron ionization on O_2, mass selected in a quadrupole mass filter, and injected into the flow tube through a Venturi inlet. The neutral reactants were introduced downstream through a finger inlet, a $^1/_8$ in. stainless

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steel tubing which enters the flow tube perpendicular to the flow and terminates at the radial center of the flow tube with an elbow directing the added gas in the upstream direction. The reactant neutral gas reacted with the ion for a known reaction time (∼2 ms) in a fast flow of He buffer gas (∼100 m s^{-1}), maintained at a total pressure of ∼0.45 Torr. A small fraction of the gas in the tube flowed through a sampling orifice, and the reactant and product ions in this flow were mass analyzed in a second quadrupole mass filter and detected by a particle multiplier. Rate constants were extracted from least-squares fits of the logarithm of the reactant ion signal versus concentration of reactant neutral. The reaction time was determined from previous time-of-flight measurements. The reactants were obtained commercially and used without further purification except for repeated freeze/thaw cycles to eliminate trapped vapors. The accuracy of the measured overall rate constants is ±25%, and the relative accuracy is ±15%.[6]

Product branching fractions were not derived in the normal fashion since one of the reaction channels produces an electron which cannot be detected by the quadrupole mass spectrometer. Branching fractions for both product channels, hydrogen abstraction and reactive detachment, were determined by comparing the decrease in the O^- reactant signal to the increase in the OH^- product ion signal. The difference represents the electron contribution from the reactive detachment channel. This method should be quite accurate since the reactant ion and product ion masses differ by only 1 Da, which essentially eliminates problems caused by mass discrimination and differing rates of diffusion. For O^- and OH^-, the ratio of the diffusion coefficients in He at 500 K is 1.1.[8]

The presence of a reactive detachment channel was also confirmed by monitoring the nose cone signal, a measure of the total ion current in the flow tube at the orifice where product and reactant ions are sampled by the downstream mass spectrometer. The nose cone signal decreased substantially upon addition of the alkane reactants due to the fact that electrons, the charged species from the reactive detachment product channel, rapidly diffuse to the walls of the apparatus.[9] For the larger alkanes, where reactive detachment is the dominant channel, the nose cone signal decayed to near zero. Monitoring the decrease in the nose cone signal as a function of neutral alkane flow rate yields an additional estimate of the product branching fractions. When the hydrogen abstraction channel was substantial, this method yielded the same branching fractions as the O^-/OH^- comparison described above. However, when the reactive detachment channel dominated, results from this method differed from the O^-/OH^- comparison due to small impurity signals of F^- (from imperfect separation in the upstream mass spectrometer). The reported results are from the O^-/OH^- comparison and are believed accurate to approximately 10%.

Results and Discussion

Total rate constants and OH^- branching percentages for the reactions of O^- with a variety of straight-chain and branched alkanes at several temperatures are presented in Table 1. Results for the CH_4 and CD_4 reactions are taken from a previous study in this laboratory.[3] Reliable rate constants could not be obtained for the reaction of n-$C_{12}H_{26}$ due to the compound's low vapor pressure. Although the reaction of O^- with CH_4 is rather slow, occurring on only 7% of collisions at 300 K, the efficiency of the other alkane reactions increases dramatically with size. For ethane, the reaction is already 40% of its collisional value at 300 K, and the rate constants for butane and the larger alkanes are at their collisional values at that temperature. Collisional rate constants were calculated using the parametrized trajectory calculations of Su and Chesnavich.[10,11] The rate constants reported here at 300 K agree with those found by Bohme and Fehsenfeld[2] within the combined uncertainty. At 500 K, the reaction efficiencies for the small alkanes are somewhat smaller than at 300 K, although the rate constants do become collisional at 500 K for pentane and the larger alkanes. Within our uncertainty, both straight-chain and branched alkanes have similar reaction efficiencies. As we have previously noted, the effect of deuteration on the reaction of O^- with CH_4 is very pronounced; the reaction rates for CH_4 and CD_4 were found to differ by up to an order of magnitude.[3] In this study, we report a much smaller effect upon deuterating propane; the reaction efficiency decreased by only 10−25%, depending on temperature.

TABLE 1: Measured Rate Constants and OH^- Product Branching Percentages for the Reactions of the Oxide Anion with Selected Alkanes as a Function of Temperature; Reaction Efficiencies (in %) Are Shown in Parentheses

	total rate constant (10^{-9} cm^3 s^{-1})			hydroxide branching percentage (% OH^- or OD^-)		
alkane	178 K	300 K	500 K	178 K	300 K	500 K
CH_4[a]	0.12 (9)	0.088 (7)	0.077 (6)	100	100	100
CD_4[a]	0.0099 (0.8)	0.0092 (0.7)	0.014 (1)	100	100	100
C_2H_6	0.74 (48)	0.59 (39)	0.39 (26)	55	60	85
n-C_3H_8	1.3 (76)	1.2 (70)	0.91 (53)	35	50	63
n-C_3D_8	1.2 (71)	1.0 (60)	0.68 (41)	30	43	54
n-C_4H_{10}		2.0 (105)	1.7 (89)		27	46
iso-C_4H_{10}		1.9 (97)	1.5 (79)		32	60
n-C_5H_{12}		2.1 (101)	1.9 (92)		21	45
iso-C_5H_{12}		2.2 (110)	2.0 (100)		25	41
neo-C_5H_{12}		2.1 (101)	2.1 (101)		97	103[c]
n-C_6H_{14}		2.3 (105)	2.5 (114)		17	30
n-C_7H_{16}		2.4 (103)	2.5 (107)		10	30
n-C_8H_{18}		2.6 (104)	2.5 (100)		9	21
iso-C_8H_{18}		2.4 (98)	2.5 (102)		38	53
n-$C_{10}H_{22}$		2.8 (104)	2.7 (100)		4	12
n-$C_{12}H_{26}$[b]					4	6

[a] Reference 3; data shown are interpolations from data measured at 173, 298, and 565 K. [b] Rate constants for the reaction of O^- with n-$C_{12}H_{26}$ could not be determined accurately because of the difficulties in working with a compound of such low vapor pressure. In addition to the OH^- product channel, a minor (∼1%) association product ion was observed at 300 K, although not at 500 K. [c] It is possible to obtain values of >100% because branching ratios were determined by comparing the increase in OH^- signal to the decrease in O^- signal. This value is within the 10% accuracy of the experiment.

In an early examination of O^- reactions with small alkanes (ethane, propane, and butane), Bohme and Fehsenfeld[2] reported that these reactions proceeded exclusively via hydrogen atom abstraction, yielding OH^- product ions and alkyl radicals. In this more comprehensive study of O^- reactions with alkanes, we find that hydrogen atom abstraction is only one of two significant reaction channels, the other being reactive detachment (production of electrons as the charge carrier). It is not surprising that the presence of the reactive detachment channel was missed in the earlier study; their measurements were made in a flowing afterglow apparatus where several ions and the neutral precursor of O^- are present simultaneously in the flow tube, which significantly complicates the chemistry. (Product balance is obscured by the presence of other ions, and electrons do not necessarily diffuse rapidly to the flow tube walls in the presence of positive ions.) In this study, we find that the product branching percentage for these reactions, representing the competition between hydrogen atom abstraction and reactive detachment, is highly dependent on both the size of the alkane

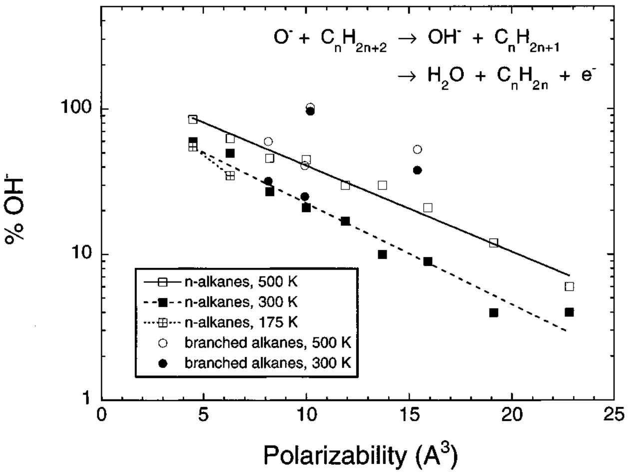

Figure 1. Percentage of OH^- produced vs alkane polarizability for the reactions of O^- with various alkanes. Normal alkanes are represented as squares and branched alkanes as circles.

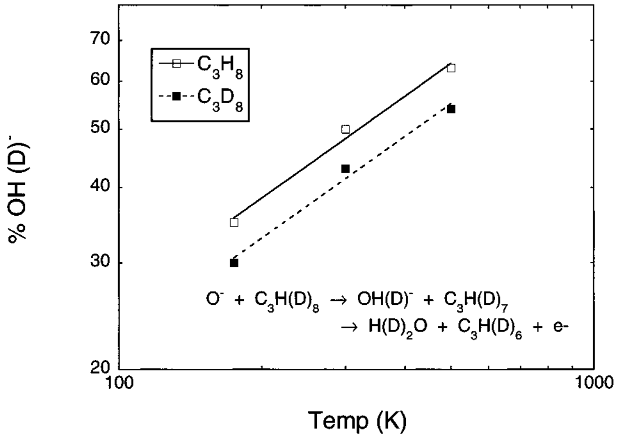

Figure 2. Temperature dependence of the percentage of OH^- produced in the reactions of O^- with C_3H_8 and C_3D_8.

and the overall alkane structure, i.e., the degree of branching within the molecule. This is demonstrated in Figure 1 where the percentage of OH^- formed from hydrogen atom abstraction is plotted as a function of the neutral alkane's polarizability. (The molecule's polarizability is roughly proportional to the number of carbons in the molecule.)

The percentage of OH^- produced from the reaction of O^- with straight-chain alkanes decreases nearly exponentially with polarizability (i.e., alkane size). Reaction with the smallest alkanes occurs largely by hydrogen atom abstraction, while reaction with larger alkanes occurs almost exclusively via reactive detachment. At 300 K, the branching fractions for the two reaction channels are approximately equal for propane. The OH^- branching fraction for the normal alkane reactions increases substantially with increasing temperature, e.g., 10–25% more OH^- is observed at 500 K than at 300 K. Deuterated propane produces slightly less $OH(D)^-$ than does propane, although the temperature dependence of the $OH(D)^-$ branching fraction is essentially $T^{0.56}$ for both reactions, as shown in Figure 2.

The competition between the hydrogen atom transfer and the reactive detachment channels is influenced not only by the alkane's size but by the overall structure of the molecule as well. This is demonstrated in Figure 1 by the four branched alkanes that were included in this study. Of those four compounds, the two with the smallest degree of branching, isobutane (2-methylpropane) and isopentane (2-methylbutane), both produced similar amounts of OH^- as their unbranched counterparts at 300 and 500 K. (Isobutane appears to produce just slightly more OH^- than does butane, although the difference is clearly within the uncertainty of our measurement.) In sharp contrast, the two compounds with a higher degree of branching react quite differently than their unbranched counterparts. The reaction of isooctane (2,2,4-trimethylpentane) produces about 30% more OH^- than does octane, while the reaction of the fully branched compound, neopentane (2,2-dimethylpropane), produces OH^- exclusively within our uncertainty, compared to only 25% OH^- production for pentane and isopentane at 300 K.

While no neutral products resulting from the reactive detachment channels were identified experimentally, the structural effects associated with the product branching percentages suggest the identity of those neutrals. One possibility is that the neutral product of the reactive detachment channel is an alcohol molecule, ROH. This would require reattachment of the OH^- product to the alkyl radical, R, accompanied by subsequent electron detachment. The fact that no measurable electron detachment is observed in the reaction of O^- with neopentane seems to rule out production of alcohols since there is no reason to suspect that alcohol production in that reaction would be any different from the other alkanes. A more likely possibility, and one that is consistent with all the data, is that the reactive detachment channel produces two neutral products, H_2O and an alkene, C_2H_{2n}. The strongest evidence for this comes from the product branching data for the reactions of O^- with the highly branched alkanes, neopentane and isooctane. These two reactions indicate that the reactive detachment channel must involve abstraction of hydrogens from two adjacent carbons within the molecule. In the case of neopentane, abstraction of an initial hydrogen atom cannot be followed by subsequent hydrogen abstraction from an adjacent carbon because the central carbon has no hydrogens. Thus, the reactive detachment channel is completely shut off for neopentane. Similarly, only half of the hydrogens in isooctane have an adjacent carbon atom that also contains hydrogen, and the reactive detachment channel for isooctane occurs on about 50% of all collisions. In contrast, all hydrogen atoms in the less branched isobutane and isopentane molecules have an adjacent carbon atom that contains hydrogen, and these molecules behave similarly to the *n*-alkanes.

For the alkanes that have adjacent hydrogens on every carbon, abstraction of hydrogens from adjacent carbons leads to the formation of a very stable alkene. The branching ratio differences between isomers in these cases are small and are possibly due to small energetic differences. The simple picture indicates that at most isooctane should produce 50% of the detachment channel. However, at room temperature we find 62% of the reaction proceeds by detachment. This indicates that there may be a preference for attachment of the O^- to a hydrogen on the less branched side of the molecule, either in the initial attachment or through migration. In a previous study of the reaction of O^- with CH_2D_2, we have shown that H/D migration is not likely. However, the larger size (i.e., longer complex lifetime) of isooctane may make migration more likely in this case.

A potential energy diagram, consistent with all the data, for the reaction of O^- with various alkanes is shown schematically in Figure 3. The reactants, O^- and RH, enter a shallow ion–dipole, induced-dipole well forming $O^-{\cdot}RH$. The complex then proceeds over a barrier to $OH^-{\cdot}R$. This pathway has been calculated in detail for the reaction of O^- with CH_4.[3] At this point, one of two things can happen. The $OH^-{\cdot}R$ complex can dissociate into products, yielding OH^- and an alkyl radical, R.

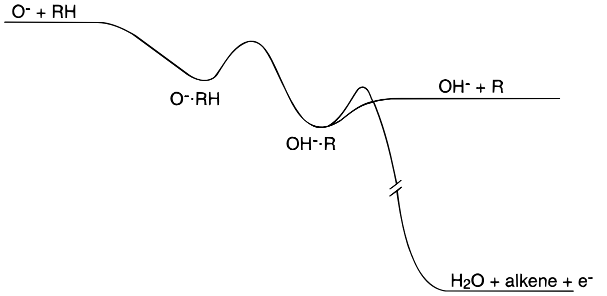

Figure 3. Schematic potential energy diagram for the reactions of O^- with alkanes.

The exothermicity of this channel is essentially constant at 40−46 kJ/mol for all alkanes larger than methane, assuming the most stable radical species is formed, e.g., secondary radicals are formed rather than primary radicals. Alternatively, the OH^- portion of the complex can abstract an H^+ from an adjacent carbon of the alkyl radical, yielding the reactive detachment products, H_2O + alkene + e^-. This reactive detachment channel is even more exothermic than the initial hydrogen atom abstraction, varying between 214 kJ/mol for ethane and 232 kJ/mol for larger alkanes such as octane.

Both wells shown in the proposed reaction pathway presumably become deeper for larger alkanes, as the polarizability of the molecule RH and the radical R increases, and this explains the increases in both the reaction efficiency and the reactive detachment branching fraction with increasing alkane size. As the wells deepen, the first barrier is probably lowered with respect to the reactant energies, leading to the observed increase in reaction efficiency. This explanation has been used successfully to explain the large isotope effect in the reaction of O^- with CH_4 and CD_4. In that case, the barrier height difference is due to zero-point vibrational energy differences. Once the well is sufficiently deep, the reaction is collisional, and deepening the well has no further effect on reactivity. For the small alkanes, the weak negative temperature dependence of the rate constants is consistent with this type of picture. The lack of a temperature dependence in the rate constants for the larger alkanes simply results from the fact that these reactions are already 100% efficient. The fact that the OH^- channel decreases exponentially with increasing alkane polarizability suggests that the deeper second well allows the OH^- portion of the $OH^-{\cdot}R$ complex additional time to abstract an H^+ before dissociating. The temperature dependence of the branching percentage is consistent with this picture because higher temperatures mean shorter complex lifetimes and, therefore, less reactive detachment.

The reaction surface shown in Figure 3 is also consistent with our observation that deuteration slightly decreases the overall reactivity in the O^- reaction with propane. The overall exothermicity to form OD^- and C_2D_5 will be less than that for OH^- and C_2H_5 due to zero-point vibrational energies. We base this on the energetics for O^- with $CH(D)_4$.[3] The main effect is due to the loss of a C−H(D) stretch in the reactants and a gain of an $OH(D)^-$ in the products. Zero-point energies also cause a slight change in the first barrier height for similar reasons, the barrier being higher for deuterium abstraction. This was explained previously in detail for the reaction of O^- with CH_4.[3] The passage over the first barrier is the rate-determining step, and thus deuteration results in a smaller rate constant, consistent with our observations.

The isotope effect in the branching ratio may have several causes. (1) Small differences in the second barrier may also exist due to zero-point energies. (2) One may have expected less detachment since D^+ abstraction may be expected to be slower than H^+ abstraction because of the larger mass. The second explanation is not consistent with the data and may therefore be at most a secondary factor and not the main one.

In summary, we have observed for the first time an electron detachment channel in the reactions of O^- with alkanes. For the small alkanes, the main reaction channel is hydrogen atom transfer, producing OH^- and an alkyl radical. The reactive detachment channel, which produces H_2O and an alkene, dominates for the larger alkanes, accounting for over 90% of the reaction for octane and larger *n*-alkanes. A simple mechanism is proposed where the first step is production of a $O^-{\cdot}RH$ complex. This complex rearranges by hydrogen abstraction to form $OH^-{\cdot}R$, which can then decompose into OH^- and R or, alternatively, form e^-, H_2O, and an alkene.

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