determined for [1], [2], and [3], along with the rate coefficient for the fast reaction between O^- and NH_3 found to proceed by hydrogen abstraction to form OH^-. The product ion OH^- accounted for essentially 100% of the disappearing O^- ions. Electron transfer will not compete since NH_3 has no affinity for electrons (2). Also, there was no indication of a residual signal at $m/e = 16$. This means that no NH_2^- was produced by the reaction and suggests that this channel for the reaction is endothermic at room temperature, implying that the electron affinity of NH_2^- is less than 1.61 eV. This observation is compatible with the electron affinity of NH_2 of 1.21 eV reported by Vedeneyev *et al.* (3). The further reaction of OH^- with NH_3 to yield NH_2^- and H_2O was not observed suggesting that the electron affinity of NH_2 may be less than 1.10 eV.

Gupta *et al.* (4) have measured the thermal (or zero field) rate constant for reaction [2] using a pulsed-beam technique. The rate of 1.0×10^{-9} determined by Gupta *et al.* at 373 °K is somewhat smaller than the value of 1.6×10^{-9} determined in the present experiment at 295 °K. There are no other published rates for the other reactions with which we may compare.

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Thermal reactions of O^- ions with saturated hydrocarbon molecules

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The thermal energy reactions of O^- ions with saturated hydrocarbon molecules have been investigated in a flowing afterglow of pure oxygen and a mixture of helium and oxygen. Hydrogen atom abstraction was found to be the dominant reaction channel. The reaction probability was found to increase for the higher members of the homologous series. The further reaction of the product OH^- ions with saturated hydrocarbon molecules was not observed. This result was used to estimate an upper limit to the electron affinity of the free radicals CH_3, C_2H_5, C_3H_7, and C_4H_9.

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The flowing afterglow technique developed in the Environmental Science Services Administration Research Laboratories has been used extensively for the study of thermal energy ion–neutral reactions of interest in aeronomy, and has been employed to investigate the reactions of O^- ions with the homologous hydrocarbon series C_nH_{2n+2}, $n = 1$ to 4. The results suggest a fairly general behavior which is that the reaction of O^- ions with saturated hydrocarbon molecules proceeds by hydrogen atom abstraction

$$[1] \qquad O^- + RH \rightarrow OH^- + R$$

and that the reaction probability for this process increases for higher members of the homologous series.

The details of the experimental apparatus, its operation, and the related data analysis have been described in detail elsewhere (1). The flow system is a stainless steel tube about 100 cm long and 8 cm in diameter in which the products of an electron impact ion source are pumped down the tube at a velocity of about 10^4 cm/s. In the present experiments either pure O_2 or O_2 in small fractional quantities in a helium buffer gas is introduced into the excitation region. The O^- ion is then produced by the dissociative ionization reaction, $e + O_2 \rightarrow O^- + O^+ + e$, and, probably to a lesser extent, the dissociative

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TABLE I

Calculated reaction probabilities for hydrogen abstraction by O^- ions

Reaction	k (22.5 °C) cm^3/s	k_c cm^3/s	Reaction probability, k/k_c
$O^- + CH_4 \rightarrow OH^- + CH_3 + 0.26\,eV$	1.0 (−10)*	1.3 (−9)	0.08
$O^- + C_2H_6 \rightarrow OH^- + C_2H_5 + 0.46\,eV$	7.0 (−10)	1.5 (−9)	0.47
$O^- + C_3H_8 \rightarrow OH^- + C_3H_7 + 0.55\,eV$	9.3 (−10)	1.7 (−9)	0.55
$O^- + n\text{-}C_4H_{10} \rightarrow OH^- + C_4H_9 + 0.59\,eV$	1.2 (−9)	1.9 (−9)	0.63

*(−10) denotes 10^{-10}.

attachment reaction, $e + O_2 \rightarrow O^- + O$. At the end of the tube the ion composition is sampled, mass analyzed by means of a quadrupole mass spectrometer, and counted. The hydrocarbon reactant gases are added downstream of the excitation region. They had the following minimum purity in mole%: methane, 99.95; ethane, 99.0; propane, 99.5; *n*-butane, 99.5. The decline of the reactant O^- ion signal as a function of hydrocarbon gas addition constitutes the raw data from which rate coefficients are determined with an absolute accuracy of about 30% and a somewhat better relative accuracy. The experiments were performed at 22.5 °C at a total steady state pressure of 0.23 Torr.

A list of the reactions investigated and the measured rate constants are given in Table I. The major product ion in each case was OH^-, indicating that hydrogen abstraction, i.e. reaction [1], is the dominant reaction channel. The reaction energies listed in Table I apply if the products are in their ground states and are given only to show that the reactions are exothermic at 22.5 °C. It is of course not unlikely that the products are formed in vibrationally excited states. Electron affinities of 1.465 and 1.78 eV were used for O and OH respectively (2). Bond energies were taken from Vedeneyev *et al.* (3).

A consideration of the ground state reaction energetics complemented by experimental observations allows an estimation of upper limits to the electron affinity of several hydrocarbon radicals. It is observed in these experiments that the OH^- ions produced by the hydrogen abstraction reactions listed in Table I do not react efficiently with the added hydrocarbon molecules (rate coefficient $\leq 10^{-12}\,cm^3/s$). This strongly suggests, but does not prove, that the reaction channel

$$OH^- + RH \rightarrow R^- + H_2O \qquad [2]$$

is endothermic since most exothermic ion–molecule reactions proceed rapidly with little or no activation energy. Accordingly, an upper limit to the value of the electron affinity of CH_3, C_2H_5, C_3H_7, and C_4H_9 may be estimated. The results are given in Table II together with values reported in the literature.

TABLE II

Estimates of the electron affinity of free radicals

Free radical	Electron affinity		
	Present result	Reference 4	Reference 5*
CH_3	<1.08	1.08, 1.1†	1.8
C_2H_5	<0.88	0.9†	1.4
C_3H_7	<0.79	0.8†	1.0
C_4H_9	<0.75		

*Calculated values (see ref. 4).

†Provisional results of Hush and Oldham (see ref. 4).

It is instructive to compare the experimentally measured reaction rate constant, k, with the theoretical collision rate constant, k_c. For an ion colliding with a neutral molecule, the theoretical collision rate constant is given by the expression

$$k_c = 2\pi e\left(\frac{\alpha}{\mu}\right)^{\frac{1}{2}} \qquad [3]$$

Here μ is the reduced mass of the reactants and α is the polarizability of the neutral reactant. Equation [3] is derived on the assumption that the total collision cross-section is determined solely by the long range ion-induced dipole interaction which results in orbiting or spiralling (6). The ratio k/k_c is a measure of the reaction probability. The calculated reaction probabilities for hydrogen abstraction from saturated hydrocarbon molecules by O^- ions are given in Table I. Polarizabilities for the neutral hydrocarbon molecules were taken from Rothe and Bernstein (7). As indicated in Table I, the experimental rate constant for the reaction of O^- with CH_4 is considerably lower than predicted by theory, and accordingly a significant fraction (0.92) of the orbiting collisions does not lead to a reaction. It is also apparent from the reaction probabilities given in Table I that the number of hydrogen abstraction reactions per orbiting collision increases for the reaction of O^- with higher members of the homologous series. Equation [3] neglects the dispersion energy between the two mutually induced dipoles in the ion–molecule collision. Inclusion of such a term in the interaction potential for O^- and the very polarizable hydrocarbon molecules could increase the theoretical collision rate constant, k_c, by as much as 10%. This in turn would decrease the reaction probability by as much as 10%.

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Photo-initiated reactions of thiols and olefins. IV. Inhibition of butene-2 isomerization by butadiene-1,3

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The kinetics of inhibition of the thiyl radical catalyzed isomerization of *cis*-butene-2 has been investigated. The results yielded the value 6.9×10^7 l mole^{-1} s^{-1} for the rate constant for CH_3S attack on butadiene. It is proposed that this technique could be generally useful in determining attack constants for conjugated olefins.

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Introduction

It was shown previously that the rate constant for thiyl radical attack on butadiene cannot be obtained from the measurement of addition rates (1). The adduct radical produced is not sufficiently reactive for thiol dehydrogenation to compete successfully with termination reactions, and no chain character was observed. This behavior is probably typical of conjugated olefins, and it appeared desirable to find a technique for determining reactivities in such cases. In earlier work on thiyl radical catalyzed isomerization of butene-2, it was found necessary to purify the olefin by gas chromatography in order to obtain consistent kinetic data over the entire concentration range used (2). The effects observed with the non-purified samples were attributed to the presence of very small quantities of butadiene in the olefin. As a result of further investigation of these effects, a new method for determining relative attack constants for conjugated olefins has been obtained.

Experimental

The techniques used were as previously described (1, 2). All results given here were obtained using a quartz reaction cell, 5 cm diameter × 10 cm length.

Results

The isomerization curves given in Fig. 1 show that addition of small amounts of butadiene to *cis*-butene-2 produces an initial retardation in rate which disappears, presumably, when the butadiene is used up. Figure 2 indicates that the initial inhibited rate of isomerization ($R_{\mathrm{ic}} = (\mathrm{d}[T]/\mathrm{d}t)_0$) is inversely proportional to the initial