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# Kinetics of the Reaction of N(<sup>4</sup>S) with Isobutane

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The kinetics of the reaction of isobutane with  $N(^{4}S)$  have been studied as a function of reactant concentration and temperature from 300 to 550 K. The initial rate of consumption of  $N(^{4}S)$  was second order in  $N(^{4}S)$  and first order in isobutane. The initiation step which best describes the results is

 $N + N + i-C_4H_{10} \rightarrow N_2 + CH_3 + 2-C_2H_7$ 

and its rate constant fits the expression

 $k = 2.26 \times 10^{17} \exp(-3890/T) \,\mathrm{dm^6 \ mol^{-2} \ s^{-1}}$ 

A mechanism is proposed for the reaction which quantitatively accounts for the consumption of  $N(^4S)$  and the production of HCN as a function of both temperature and time. HCN arises in this mechanism from reactions of  $N(^4S)$  with CH<sub>3</sub>, 2-C<sub>3</sub>H<sub>7</sub> and other alkyl radicals formed in subsequent reactions.

The reactions of N(<sup>4</sup>S) with saturated hydrocarbons have been studied extensively, particularly during the period 1950-1965 when it was thought that such reactions might provide information on the nature of the reactive species in 'active nitrogen'. The kinetic work on these reactions prior to 1971 has been reviewed<sup>1-3</sup> and they appear not to have been studied more recently. The only work dealing specifically with the kinetics of the reaction of N(4S) with isobutane was reported by Back and Winkler<sup>4</sup> in 1954 in which secondorder rate constants were reported at two temperatures. The main product of the reaction was HCN and an activation energy of 13 kJ mol<sup>-1</sup> was reported. In general, the reactions of alkanes with N(4S) are very slow, producing HCN as the main product. The rate constants reported have been obtained on the assumption that the reactions obey overall second-order kinetics, first order in N(4S) and first order in the organic reactant. When the temperature dependence of these reactions has been measured, the activation energies were found to be of the order of 20-30 kJ mol<sup>-1</sup>, a value comparable to that for reactions of O(<sup>3</sup>P) with alkanes. However, the Arrhenius pre-exponential factors were several orders of magnitude smaller than those typical of the corresponding  $O(^{3}P)$  reactions.

A series of experiments on the reactions of  $N(^4S)$  with alkanes indicated that these reactions were strongly catalysed by trace amounts of alkenes present in the commercial samples of the alkanes.<sup>3</sup> When these impurities were removed, most of the reactivity toward  $N(^4S)$  disappeared but this reactivity could be restored and enhanced by adding a small concentration of atomic hydrogen to the stream containing  $N(^4S)$ . It was concluded that much of the previously reported chemical reaction of  $N(^4S)$  with alkanes was a result of catalysis by atomic hydrogen produced in the reactions of  $N(^4S)$  with alkene impurities in the starting materials.

Isobutane was unusual among the lower molecular weight alkanes examined in that some measurable reaction with  $N(^4S)$  remained after removal of the alkene impurities. Further efforts to purify the isobutane more rigorously produced no further reduction in reactivity. The reaction was second order in  $N(^4S)$  and first order in isobutane at room temperature. However, a detailed kinetic study was not carried out at that time.

Our interest in the kinetics of this reaction arises from two sources. It has been suggested that the reactions of  $N(^4S)$  with alkanes are similar to those of  $O(^3P)$ .<sup>2</sup> However, the indication of third-order initiation in the  $N(^4S)$  reaction casts this suggestion in a new light in view of the known second-order initiation kinetics of the reactions of  $O(^{3}P)$  with alkanes. A re-examination of the kinetics of reactions of N(4S) with alkanes seemed to be necessary in order to extract fundamental information on the ways in which attack by N(<sup>4</sup>S) on organic compounds differs from the corresponding reactions of other atomic and free-radical species. A second objective is related to our continuing interest in the kinetics and mechanism of production of CN emission in reactions of N(<sup>4</sup>S) with organic compounds. For example, the reactions of  $N(^{4}S)$ with simple alcohols, which we have studied,<sup>5,6</sup> produce proportionately much more CN violet emission than is apparent in the reaction of isobutane with N(4S). Before the kinetics of CN production in this reaction can be examined, the kinetics of the overall reaction of N(4S) with isobutane must be known and a reasonable mechanism must be available for the reaction.

#### Experimental

The flow system and many of the experimental methods used in this work have been described in earlier publications<sup>5,6</sup> and are summarized here. Nitrogen (Linde, 99.99%) was purified by passing it through furnaces packed with copper and with copper oxide and then through a trap cooled with liquid nitrogen. This procedure has been shown to remove traces of hydrocarbons,  $H_2$ ,  $O_2$  and water<sup>6</sup> efficiently, which might otherwise produce enough atomic hydrogen or oxygen to catalyse the reactions of N(<sup>4</sup>S).<sup>2,3</sup> The N(<sup>4</sup>S) atoms were produced by a microwave-powered electrical discharge in nitrogen. The discharge tube was separated from the cylindrical reaction vessel by a 500 cm<sup>3</sup> bulb which allowed excited species formed in the discharge to decay efficiently before the gas stream entered the reaction vessel. This was necessary to avoid possible interference by energy transfer from such excited species which may have affected some of the earlier work on reactions of N(4S) in which the organic reactant was added quite close to the discharge. The concentration of N(<sup>4</sup>S) was measured by a gas-phase titration with NO using fixed inlets at the ends of the reaction vessel or a moveable inlet which could be positioned as desired along the axis of the reaction vessel. The reaction vessel was enclosed in an electrically heated furnace for experiments at elevated temperatures. The temperature was measured with a calibrated copper-constantan thermocouple located in the tip of the moveable reactant inlet. Measurements of the temperature as

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a function of distance along the axis of the reaction vessel showed that the temperature within the reaction zone used in the kinetic work was constant to within 2 °C or less.

Isobutane (Matheson, Instrument grade) was found by gas chromatographic analysis to contain ca. 0.06% propene. This was efficiently removed by passing the isobutane through a solution of  $HgSO_4$  in dilute sulphuric acid<sup>7</sup> followed by removal of water by passing it over silica gel. It was then further purified by bulb-to-bulb distillations in which only the middle fraction was retained.

HCN, formed as a reaction product, was measured by collecting it for a known length of time in traps cooled with liquid nitrogen. It was then absorbed in ammonia solution and this solution was titrated with AgNO<sub>3</sub>.<sup>8</sup> The reaction time in these experiments was varied by quenching the reaction with NO at various distances from the reaction vessel inlet.

Rate constants were measured experimentally from the initial rates of loss of  $N(^4S)$ . The reaction vessel was coated with boric acid to inhibit heterogeneous recombination of  $N(^4S)$ . There was no indication of a measurable contribution from such heterogeneous recombination under the conditions of our experiments. Further estimation of rate constants and evaluation of reaction mechanisms was achieved by numerical integration of the relevant differential equations with a computer program which we have used elsewhere.<sup>9</sup>

#### **Results and Discussion**

The only carbon-containing product found in the reaction of isobutane with  $N(^4S)$  was HCN. Fig. 1 presents representative results for the variation of HCN and  $N(^4S)$  concentrations with reaction time when isobutane is in substantial excess of  $N(^4S)$ . As is often observed in reactions of  $N(^4S)$  with organic compounds,<sup>1</sup> the yield of HCN was much less than the consumption of  $N(^4S)$ .

The slopes of tangents to the initial parts of curves, such as those in Fig. 1, were used to obtain initial rates of loss of  $N(^4S)$  as functions of the initial concentrations of both  $N(^4S)$ and isobutane, and the initial rates of formation of HCN as a function of the initial concentration of isobutane. The comparatively small yield of HCN prevented accurate measurement of its rate of formation over a significantly wide range of initial concentrations of  $N(^4S)$ . The initial rates were then used as indicated in Fig. 2 to obtain the orders of the reaction with respect to isobutane and  $N(^4S)$ . It is clear from these results that the order of reaction with respect to isobutane is unity when measured both from the loss of  $N(^4S)$  and from the production of HCN. The order of the reaction with



Fig. 1 Representative variation of  $[N(^{4}S)]$  (O) and [HCN] ( $\bullet$ ) with time;  $[C_{4}H_{10}] = 1.83 \times 10^{-6} \text{ mol dm}^{-3}$ , T = 430 K



Fig. 2 log-log plots for determination of reaction order: ( $\bigcirc$ ) X = isobutane, rate = -d[N]/dt; ( $\bigcirc$ ) X = N(<sup>4</sup>S), rate = -d[N]/dt; ( $\triangle$ ) X = isobutane, rate = d[HCN]/dt

respect to  $N(^4S)$  is two, based on the measured initial rates of loss of  $N(^4S)$ .

With a sufficiently large excess of isobutane over N(4S), the concentration of isobutane remains effectively constant and the consumption of N(4S) early in the reaction will be pseudo-second order. Analysis of the early part of the N(4S) loss curves under these conditions yields a second-order rate constant, incorporating this effectively constant concentration of isobutane. These second-order rate constants include two terms. The first of these depends on the first power of the isobutane concentration and combines both the component of N(<sup>4</sup>S) removal attributed to use of isobutane as a third body and any chemical processes involving N(4S) to the second order and isobutane. The second term represents recombination of  $N(^4S)$  using  $N_2$  as the third body. While a contribution from first-order heterogeneous recombination of  $N(^{4}S)$  might be expected in principle, the boric acid coating on the reactor, referred to earlier, made this insignificant. The concentration of isobutane used in our experiments was sufficiently large and the pressure was sufficiently small that the term for recombination of  $N(^4S)$  using  $N_2$  as a third body was also negligible. The third-order rate constants for the reaction of N(<sup>4</sup>S) with isobutane were therefore calculated by dividing the second-order rate constants, obtained from the measured rate of loss of N(4S), by the concentration of isobutane. These rate constants are presented in Table 1 and are plotted in Arrhenius form in Fig. 3 from which an activation energy of  $28.4 \pm 4\%$  kJ mol<sup>-1</sup> and a pre-exponential factor of  $3.0 \times 10^{17} \pm 30\%$  dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup> are calculated.



Fig 3 Temperature dependence of the rate constant for the reaction of  $N(^4S)$  with isobutane: ( $\bigcirc$ ) experimental rate constants; ( $\bigcirc$ ) fitted absolute rate constants

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<sup>*a*</sup> 1 Torr  $\approx$  101 325/760 Pa.

overall reaction to be:

radical products.

 Table 1
 Summary of kinetic data

T/K	pressure /Torr <sup>a</sup>	[N( <sup>4</sup> S)]/10 <sup>-7</sup> mol dm <sup>-3</sup>	$[i-C_4H_{10}]/10^{-7}$ mol dm <sup>-3</sup>	$k/10^{13} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
303	0.995	7.06	19.9	0.314
303	0.953	9.91	19.2	0.336
334	1.27	1.65	18.3	1.16
355	1.86	1.59	12.5	1.48
357	1.62	1.45	18.1	2.55
375	1.67	1.72	15.7	2.94
379	1.38	1.52	17.7	3.79
394	1.14	1.14	13.7	7.05
410	1.11	0.778	6.68	12.3
413	1.10	1.02	9.31	7.67
415	2.38	1.06	4.70	10.0
431	1.12	0.764	6.41	9.64
433	1.12	0.885	9.04	10.7
450	1.11	0.863	6.05	13.3
450	1.11	0.990	8.57	10.2
469	1.17	1.08	12.1	16.1
488	1.09	1.06	7.71	32.1
493	1.09	1.01	5.39	45.2
552	0.887	2.86	12.0	89.1

The kinetic analysis presented above applies only to the

early part of the reaction under conditions of excess iso-

butane. At longer reaction times, while the reaction remains

second order in N(4S) and first order in isobutane, the

numerical value of the experimental third-order rate con-

stant, calculated from the consumption of N(4S), increases

somewhat, indicating a catalytic effect similar to that noted in

other work.<sup>3</sup> Moreover, the observation in our experiments

of a significant activation energy for the consumption of

N(<sup>4</sup>S), as well as the appearance of HCN as a reaction

product, suggests a more complex process than simple homo-

geneous recombination of N(4S) using isobutane as a third

body. Development of a mechanism for the overall reaction

must provide for production of an intermediate, presumably

in a reaction having a significant activation energy, which can

then produce HCN. The mechanism must also take into

account the fact that only a small proportion of the N(<sup>4</sup>S)

consumed in the reaction leads to HCN. Use of reasonable

values of kinetic parameters for the reactions in the mech-

anism should provide agreement with the experimentally

measured time dependence of the concentrations of N(4S) and

HCN. We consider the most plausible initiation step for the

 $N + N + i-C_4H_{10} \rightarrow N_2 + CH_3 + 2-C_3H_7$ 

This would be consistent with the observed kinetic orders. It

would then logically be followed by reactions with the alkyl

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$$N + CH_3 \rightarrow HCN + 2H$$
 (2)

$$N + 2 - C_3 H_7 \rightarrow 2CH_3 + HCN$$
(3)

The hydrogen atoms formed in reaction (2) would react further with the isobutane as follows

$$H + i - C_4 H_{10} \rightarrow H_2 + (CH_3)_2 CHCH_2$$
 (4)

$$H + i - C_4 H_{10} \rightarrow H_2 + (CH_3)_3 C$$
 (5)

and would recombine at the walls of the reactor.

$$H \to 1/2H_2 \tag{6}$$

The butyl radicals formed in reactions (4) and (5) would also react with  $N(^{4}S)$  in a series of reactions such as the following:

$$N + (CH_3)_2 CHCH_2 \rightarrow HCN + H + 2 \cdot C_3 H_7$$
(7)

$$N + (CH_3)_3 C \rightarrow CH_3 CN + 2CH_3$$
(8)

While we did not detect  $CH_3CN$  among the reaction products, its concentration would have been much smaller than that of HCN and it is likely that it would not have been detectable with our gas chromatograph. There is evidence from other work<sup>5</sup> that reactants that are able to produce  $(CH_3)_3C$  radicals react with N(<sup>4</sup>S) to give small yields of  $CH_3CN$ .

The complete model, together with the kinetic parameters used, is presented in Table 2. Reactions (9) and (10) are included largely for completeness, although they are likely to become significant for recombination of N(4S) only at small concentrations of isobutane. Rate constants for reactions of N(<sup>4</sup>S) with organic free radicals were assumed all to have the same Arrhenius parameters as those reported recently for reaction (2).<sup>12</sup> These reactions have such large rate constants in comparison with the rate-determining step, reaction (1), that the results were quite insensitive to substantial changes in the values of their rate parameters. The effect of the reactions of N(<sup>4</sup>S) with organic free radicals is to make the rate constant measured from the rate of consumption of  $N(^{4}S)$ larger than the absolute rate constant by a stoichiometric factor. The absolute rate constant for reaction (1) was adjusted downward from the experimental value until the calculated and experimental plots of N(4S) consumption were in reasonable agreement. The choice of rate constant for reaction (6) had a small effect on the curvature of the plots of  $N(^{4}S)$  consumption via reactions (4), (5), (7) and (8). The value of  $k_6$  was selected to provide improved agreement with experiment at longer reaction times. This value varied somewhat from one experiment to another, presumably as a reflection of variations in the catalytic efficiency of the reactor surface for recombination of atomic hydrogen, and the values

Table 2 Kinetic model

(1)

reaction	A <sup>a</sup>	$\Delta E_{\rm s}/{\rm kJ}~{\rm mol}^{-1}$	ref.
$(9)  N + N + N_2 \rightarrow N_2^* + N_2$	$8.36 \times 10^{8}$	-4.08	10
(10) $N + N_2^* \rightarrow \tilde{N}_2 + \tilde{N}_2$	$1.00 \times 10^{10}$	0.0	11
(1) $N + N + C_4 H_{10} \rightarrow CH_3 + C_3 H_7 + N_2$	$2.26 \times 10^{17}$	32.3	this work
(2) $N + CH_3 \rightarrow HCN + 2H$	$2.00 \times 10^{11}$	2.7	12
(3) $N + C_3H_7 + 2CH_3 + HCN$	$2.00 \times 10^{11}$	2.7	see text
(4) $H + C_4 H_{10} \rightarrow H_2 + (CH_3)_2 CHCH_2$	$1.00 \times 10^{11}$	35.1	13
(5) $H + C_4 H_{10} \rightarrow H_2 + (CH_3)_3 C$	$1.26 \times 10^{11}$	30.5	13
(7) $N + (CH_3)_2 CHCH_2 \rightarrow HCN + H + C_3H_7$	$2.00 \times 10^{11}$	2.7	see text
(8) $N + (CH_3)_3 C \rightarrow CH_3 CN + 2CH_3$	$2.00 \times 10^{11}$	2.7	see text
$(6)  \mathbf{H} \to 1/2\mathbf{H}_2$	$1.00 \times 10^{2}$	0.0	see text

<sup>a</sup> The Arrhenius pre-exponential factors use the units mol, dm<sup>3</sup> and s.

of  $k_6$  should probably be regarded as a means of correcting for changing surface conditions rather than as having any fundamental quantitative significance for the reaction being studied. The dependence of the kinetic behaviour on the value selected for  $k_6$  supports the contention that reactions of atomic hydrogen play a significant role in the reaction. The values of the absolute rate constants,  $k_1$ , for reaction (1) obtained from the fitting procedure outlined above are plotted in Fig. 3. The resulting Arrhenius plot is nearly parallel to that for the experimental rate constants and yields an activation energy of  $32.3 \pm 4\%$  kJ mol<sup>-1</sup> with a preexponential factor of  $2.3 \times 10^{17} \pm 30\%$  dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup>. The stoichiometric coefficient,  $k_{measured}/k_1$ , had a nearly constant value of 4.5 with a barely distinguishable decreasing tendency with increasing temperature.

The model was also used to calculate the yields of HCN to be expected for a range of reaction conditions for which experimental yields of HCN had been measured. These results are plotted in Fig. 4 as calculated yield against measured yield because many of the experiments covered differing temperatures, reaction times and initial concentrations of reactants. The correlation between the predictions of the model and the experiments is excellent, giving a slope of unity within the experimental uncertainty of the results and passing through the origin. This is an independent validation of the reliability of the rate constants used in the model since the HCN yields were not used in the calculation of experimental rate constants or in the fitting of the model to the experimental data.

The model presented above assumes that the initiation step is

$$N + N + i - C_4 H_{10} \rightarrow N_2 + C H_3 + 2 - C_3 H_7$$
 (1)

An alternative possibility would be

$$\mathbf{N} + \mathbf{N} + \mathbf{N}_2 \rightarrow \mathbf{N}_2^* + \mathbf{N}_2 \tag{9}$$

where  $N_2^*$  is an excited nitrogen molecule, possibly  $N_2(A^3\Sigma_u^+)$ , followed by energy transfer from  $N_2^*$  to isobutane.

$$N_2^* + i - C_4 H_{10} \rightarrow N_2 + C H_3 + 2 - C_3 H_7$$
 (11)

Reactions such as (11) have been studied experimentally<sup>14,15</sup> and good estimates are available for the relevant rate constants. This possibility was examined by replacing reaction (1) with reaction (11) in the model and determining the value of  $k_{11}$  that would be required to produce the experimentally measured extent of reaction. In all cases, the value of  $k_{11}$ 



Fig. 4 Correlation of HCN concentrations calculated using the model with those measured experimentally

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required was orders of magnitude larger than would be consistent with reasonable estimates from the literature. Moreover, the quality of the fit to the plots of  $N(^4S)$  consumption was not as good as was possible with reaction (1). Reactions such as (11) also do not normally have activation energies of the magnitude found experimentally in this system and it was not possible to reproduce the experimental temperature dependence of the rate of consumption of  $N(^4S)$  by other reasonable reactions. For these reasons, reaction (1) is considered to be the more likely initiation step for the reaction of  $N(^4S)$  with isobutane.

The results reported here indicate that the reaction of isobutane with N(<sup>4</sup>S) is third order overall with a second-order dependence on N(<sup>4</sup>S). In this respect, it differs both from the reactions of  $O({}^{3}P)$  with saturated hydrocarbons and from the kinetic behaviour previously assumed for the reactions of saturated hydrocarbons with N(4S). It is also consistent with the general tendency for N(4S) to react by forming an addition complex<sup>1,2,5</sup> which then decomposes to form products, since nitrogen atoms would have difficulty adding to the sp<sup>3</sup> carbon atoms in saturated hydrocarbons. The difficulties associated with abstraction of a hydrogen atom by  $N(^{4}S)$ have also been discussed<sup>1,2</sup> and would make that route unlikely as well. The observation of a significant activation energy for the reaction presumably indicates that recombination of N(4S) using isobutane as a third body does not deposit enough energy in a C-C bond to result in decomposition of the hydrocarbon so that additional energy must be supplied thermally. The measured activation energy suggests that ca. 35% of the energy released by N(4S) recombination is used in breaking the C-C bond in isobutane, thus initiating the subsequent chemical reactions. The results do not support initiation of the reaction by energy transfer from an electronically excited molecule such as  $N_2(A^{-3}\Sigma_u^+)$ .

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