Canadian Journal of Chemistry

Issued by The National Research Council of Canada

VOL. 30

NUMBER 12

THE REACTION OF ACTIVE NITROGEN WITH PROPYLENE¹

By G. S. TRICK AND C. A. WINKLER

ABSTRACT

The reaction of nitrogen atoms with propylene has been found to produce hydrogen cyanide and ethylene as the main products, together with smaller amounts of ethane and propane and traces of acetylene and of a C₄ fraction. With excess propylene, the nitrogen atoms were completely consumed and for the reaction at 242°C., 0.77 mole of ethylene was produced for each mole of excess propylene added. For reactions at lower temperatures, less ethylene was produced. The proposed mechanism involves formation of a complex between the nitrogen atom and the double bond of propylene, followed by decomposition to ethylene, hydrogen cyanide, and atomic hydrogen. The ethylene would then react with atomic nitrogen in a similar manner.

INTRODUCTION

The reactions of active nitrogen with ethylene (7, 8) and with methane and ethane (4) have been discussed in previous papers from this laboratory. The reaction with propylene has now been studied, with the results recorded in the present paper. As before, the interpretation assumes the reactive species to be atomic nitrogen.

EXPERIMENTAL

The investigation was made using an apparatus which was essentially identical with that described previously (4, 7). The reaction products were analyzed by distilling the hydrocarbon fraction from the hydrogen cyanide at -85° C., after which the hydrocarbon fraction, containing small quantities of hydrogen cyanide, was separated into C₂, C₃, C₄, and HCN fractions by distillation in a column of the type described by LeRoy (10). The still was modified so that it was possible to distill directly from the still-pot to a condenser cooled by liquid nitrogen. A Toepler pump was used only to remove the last traces of one fraction before the next fraction was distilled off. By this procedure it was possible to obtain a sufficiently large sample to determine the unsaturates by the Bone and Wheeler method. The unsaturates were removed by absorption in a sulphuric acid solution of mercuric sulphate. Acetylene was absorbed in alkaline potassium iodomercurate.

Hydrogen cyanide from the first fraction was determined by weight and also by titration in alkaline solution with silver nitrate. To the value so obtained was added the amount of hydrogen cyanide analyzed by the LeRoy still.

Manuscript received March 20, 1952.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the Defence Research Board, Ottawa. Permission of the Defence Research Board to publish this paper is gratefully acknowledged.

RESULTS

With increase in propylene flow rate at constant nitrogen atom input, the yield of hydrogen cyanide increased almost linearly until it attained a constant value (within $\pm 5\%$) at a propylene flow rate beyond which consumption of nitrogen atoms was presumably complete. Complete consumption of nitrogen atoms was observed at a different flow rate of propylene when the reaction vessel was cleaned and re-poisoned with metaphosphoric acid. Presumably this was due to differences in nitrogen atom concentrations as a result of different wall conditions in the reaction vessel. For this reason, a complete series of experiments was made without altering the conditions of the walls. The curves for two different series of experiments are shown in Fig. 1.



FIG. 1. Rate of formation of various products in the nitrogen atom – propylene reaction, as a function of the propylene flow rate.

Measurements of atom concentrations were made using a Wrede gauge at the entrance and exit of the reaction bulb. A small decrease in concentration of nitrogen atoms across the bulb was noted but the average value of the nitrogen atom concentration as measured by the Wrede gauge was always 15 to 25% greater than that inferred from the amount of hydrogen cyanide produced at propylene flow rates where consumption of nitrogen atoms was complete. Owing to possible errors in the Wrede gauge measurements (11) and its lack of sensitivity the hydrogen cyanide yield with complete nitrogen atom consumption probably gives the more accurate estimate of the nitrogen atom concentration.

The main product of the reaction, apart from hydrogen cyanide, was found to be ethylene. Smaller quantities of propane and ethane and traces of acetylene (about 1% of the propylene input) were also found. A C₄ fraction, to the extent of about 2% of the propylene input, was found to consist mainly of unsaturated material. The average carbon balance accounted for about 96% of the propylene input.

In Table I are summarized the results of a series of experiments made at $242 \pm 3^{\circ}$ C. The yield of hydrogen cyanide is plotted in Fig. 1 and is seen to correspond to an average nitrogen atom flow of 9.7×10^{-6} moles per sec.

Propylene flow	Yield of products—moles/sec. \times 10 ⁶								
	HCN	C ₂	C ₂ H ₄	C ₂ H ₆	Сз.	C₃H6	C₃H ₈		
$\begin{array}{c} 2.12\\ 3.29\\ 3.46\\ 4.12\\ 5.08\\ 5.12\\ 5.24\\ 6.55\\ 7.01\\ 9.32 \end{array}$	$\begin{array}{c} 5.40\\ 7.80\\ 9.30\\ 9.50\\ 9.50\\ 10.2\\ 9.7\\ 10.5\\ 9.66\\ 9.60\end{array}$	$\begin{array}{c} 0.25\\ 0.32\\ 0.33\\ 0.69\\ 1.62\\ 0.90\\ 1.58\\ 2.50\\ 2.95\\ 4.60\end{array}$	$\begin{array}{r} - \\ 0.29 \\ 0.29 \\ 0.57 \\ 1.40 \\ 0.68 \\ - \\ 2.25 \\ 2.68 \\ 4.31 \end{array}$	$\begin{matrix} - & - \\ 0.03 \\ 0.04 \\ 0.12 \\ 0.22 \\ 0.22 \\ - \\ 0.25 \\ 0.27 \\ 0.29 \end{matrix}$	$\begin{array}{c} 0.08\\ 0.25\\ 0.27\\ 0.26\\ 0.68\\ 0.75\\ \hline \\ 1.18\\ 1.52\\ 2.20\\ \end{array}$	$\begin{array}{c} & -\\ & 0.19\\ & 0.21\\ & 0.20\\ & 0.43\\ & 0.41\\ & -\\ & 0.83\\ & 1.21\\ & 1.75\end{array}$	$\begin{array}{c} - \\ 0.06 \\ 0.06 \\ 0.25 \\ 0.34 \\ - \\ 0.35 \\ 0.31 \\ 0.45 \end{array}$		

TABLE I PRODUCTION OF HYDROGEN CYANIDE AND OTHER PRODUCTS AT VARIOUS PROPYLENE FLOWS (TEMP = $242 \pm 3^{\circ}$ C.)

In Table II are shown the results of another series of experiments made at $96 \pm 2^{\circ}$ C. All these experiments were made with a propylene flow greater than that corresponding to complete nitrogen atom consumption, with an average yield of hydrogen cyanide of 8.0×10^{-6} moles per sec.

In Fig. 1 is shown the total yield of C_2 hydrocarbons (ethane and ethylene) as a function of the rate of addition of propylene for experiments at the two

TABLE II PRODUCTION OF HYDROGEN CYANIDE AND OTHER PRODUCTS AT VARIOUS PROPYLENE FLOWS (TEMP. = $96 \pm 2^{\circ}$ C.)

Propylene	Yield of products—moles/sec. \times 10 ⁶								
now	HCN	C ₂	C₂H₄	C ₂ H ₆	C ₃	C ₃ H ₆	C ₃ H ₈		
$\begin{array}{r} 3.43 \\ 4.05 \\ 4.52 \\ 5.17 \\ 5.78 \\ 5.82 \\ 9.02 \end{array}$	8.1 8.0 8.7 7.6 8.0 8.0 8.2	$\begin{array}{c} 0.30 \\ 0.86 \\ 0.61 \\ 1.24 \\ 1.31 \\ 1.35 \\ 2.60 \end{array}$	$\begin{array}{r} 0.27\\ 0.77\\ 0.51\\ 1.12\\ 1.18\\ 1.22\\ 2.41\end{array}$	$\begin{array}{c} 0.03 \\ 0.09 \\ 0.10 \\ 0.12 \\ 0.13 \\ 0.13 \\ 0.19 \end{array}$	$\begin{array}{r} 0.28 \\ 0.58 \\ 0.60 \\ 1.35 \\ 1.80 \\ 1.40 \\ 3.50 \end{array}$	$\begin{array}{c} 0.1\acute{6}\\ 0.36\\ 0.31\\ 1.02\\ 1.38\\ 0.98\\ 2.90 \end{array}$	$\begin{array}{c} 0.12\\ 0.22\\ 0.29\\ 0.33\\ 0.42\\ 0.42\\ 0.60\\ \end{array}$		

CANADIAN JOURNAL OF CHEMISTRY. VOL. 30

temperatures. It can be seen that the rate of production of C_2 products is essentially linear with the rate of introduction of propylene, once conditions are reached corresponding to complete removal of nitrogen atoms. The C_2 yield at the higher temperature is about 65% greater, on the average, than at the lower temperature.

In Fig. 1 are also shown the yields of saturated products and recovered C_3 hydrocarbons (propane and propylene).

DISCUSSION

The absence of any product containing nitrogen, other than hydrogen cyanide, would seem to eliminate the possibility that any nitrogen-containing complex of appreciable stability is formed, or that hydrogen is abstracted from the propylene molecule by the nitrogen atom to form the NH radical.

The appearance of C_2 hydrocarbons as the principal product of the reaction leaves little doubt that the main reaction is removal of one carbon atom by an attacking nitrogen atom. The fact that ethylene is considerably more reactive than ethane towards nitrogen atoms suggests that the initial attack is at the carbon-carbon double bond, rather than at the single bond, to form a complex which may revert to the reactants or decompose according to:

$$CH_{3}CH = CH_{2} + N \rightarrow [CH_{3} - CH - CH_{2}] \rightarrow CH_{3}CH + CH_{2}N \quad (1)$$

which would then be followed by:

$$H_2 N \to H C N + H . \tag{2}$$

It is interesting, perhaps, that compounds such as CH_2N have been suggested by Geib and Harteck (6) as intermediates in the production of CH_3N in the reaction between hydrogen atoms and hydrogen cyanide at liquid nitrogen temperatures. The ethylidene radical has been postulated by various workers as an intermediate in free radical reactions. For example, Bawn and Dunning (1) and Bawn and Milsted (2) found ethylene as a product of the reaction of ethylidene dibromide with excess sodium atoms. Since the addition of molecular hydrogen did not produce any ethane, they considered the ethylidene radical to rearrange very rapidly to ethylene, thus:

С

$$CH_3CH \to CH_2 = CH_2.$$
(3)

The reaction of ethylene with nitrogen atoms could then proceed as previously outlined (8), the main reactions being:

$$CH_2 = CH_2 + N \rightarrow [activated complex] \rightarrow HCN + CH_3,$$
 (4)

$$CH_3 + N \rightarrow HCN + 2H$$
. (5)

However, the attack on ethylene by a nitrogen atom to form the methylene radical would correspond more closely to the formation of the ethylidene radical from propylene; thus:

$$CH_2 = CH_2 + N \rightarrow [CH_2 - CH_2] \rightarrow CH_2N + CH_2, \qquad (6)$$

918

$$CH_2N \to HCN + H$$
 (2)

and these reactions might be followed by:

$$CH_2 + N \rightarrow HCN + H$$
. (7)

The methylene radical is electronically similar to, but more stable than, the ethylidene radical (2).

Owing to the conflicting values of bond dissociation energies found in the literature and the absence of a well established dissociation energy for the nitrogen molecule (5) it is difficult to make an estimate of the heat of reaction for the mechanism proposed. It might be suggested that the rearrangement of the ethylidene radical to ethylene takes place in the activated complex and this extra energy of stabilization would be available for decomposition of the complex. However, no such energy of rearrangement is available in reaction (6) between nitrogen atoms and ethylene. Since nitrogen atoms attack both propylene and ethylene with velocities of the same order of magnitude, it may be concluded that the ethylidene radical is formed in the free state and that its energy of rearrangement is not available to aid the decomposition of the complex in reaction (1).

It is also possible that the initial reaction of nitrogen atoms with propylene could be:

$$CH_{3}CH = CH_{2} + N \rightarrow [CH_{3}CH - CH_{2}] \rightarrow HCN + CH_{3}CH_{2} \qquad (8)$$

which is energetically more favorable than reaction (1). The ethyl radical then could undergo further reaction with nitrogen atoms. However, to obtain considerable ethylene as a product, it would be necessary for the ethyl radicals to be comparatively inactive towards nitrogen atoms and to disproportionate

$2CH_3CH_2 \rightarrow CH_2 = CH_2 + CH_3CH_3$.

This would lead to equal quantities of ethane and ethylene formed in the reaction chamber and since the nitrogen atoms remaining would react more rapidly with the unsaturate, more ethane than ethylene should be trapped out. This is contrary to the observed behavior, and it may be concluded, therefore, that reaction (8) is of little significance.

The saturated products obtained when nitrogen atoms attack propylene are probably formed by hydrogenation of the corresponding olefin, in reactions of the type (12)

$$C_n H_{2n}$$
 + H $\rightarrow C_n H^*_{2n+1}$, ·

$$C_n H^*_{2n+1} + H_2 \rightarrow C_n H_{2n+2} + H$$

where $C_n H^*_{2n+1}$ represents a radical containing the heat of hydrogenation.

In addition to their reaction with nitrogen atoms to form hydrogen cyanide, methylene radicals may react with propylene to form the butene detected in the products, or may suffer hydrogenation to methane (3) sufficiently to account for the small deficiency in the carbon balance. The possible reactions of the methyl-

ene radical are difficult to establish since its reactivity depends upon whether it occurs in the singlet or triplet state (9).

The traces of acetylene found in the reaction products may be readily explained by slight dehydrogenation of ethylene (cf. 13, p. 262).

From the preceding remarks, it seems reasonable to represent the main reactions involving consumption of nitrogen atoms by the sequence

$$C_{3}H_{6} + N \xrightarrow{k_{1}} C_{2}H_{4} + HCN + H ,$$

$$C_{2}H_{4} + N \xrightarrow{k_{2}} CH_{2} + HCN + H , .$$

 $CH_2 + N \xrightarrow{k_3} HCN + H$.

From rate expressions of the usual form for the rates of reaction of propylene and ethylene, it is readily shown that

$$\frac{d[C_2H_4]}{d[C_3H_6]} = \frac{k_2[C_2H_4]}{k_1[C_3H_6]} - 1.$$

On integration and evaluation of the integration constant for the condition that $[C_2H_4] = 0$ when $[C_3H_6] = [C_3H_6]_0$,

$$[C_{2}H_{4}]_{1} = \frac{[C_{3}H_{6}]_{0} \left(\frac{[C_{3}H_{6}]_{1}}{[C_{3}H_{6}]_{0}}\right)}{1 - \frac{k_{2}}{k_{2}}} \left\{ \left(\frac{[C_{3}H_{6}]_{1}}{[C_{3}H_{6}]_{0}}\right)^{(k_{2}/k_{1}) - 1} - 1 \right\}$$

where $[C_3H_6]_0$ is the concentration of propylene at the inlet to the reaction vessel (propylene flow rate) and $[C_2H_4]_1$ and $[C_3H_6]_1$ are the concentrations of ethylene and propylene respectively at the outlet of the reaction vessel when nitrogen atom consumption is complete. These latter concentration terms may be expressed as the amounts of ethylene and propylene trapped out in unit reaction time.

Values of $[C_2H_4]_1$ may now be calculated for different assumed values of k_2/k_1 and different values of $[C_3H_6]_0$, the input flow rate of propylene. In Table III are shown values of $[C_2H_4]_1$ for k_2/k_1 ratios of 0.75 and 1.75 calculated from the data at 96° and 242°C. respectively. The total C_3 yields have been used for $[C_3H_6]_0$ in making the calculations, since the propane included in this figure essentially represents, in all probability, propylene that remained unreacted with nitrogen atoms and was subsequently hydrogenated. In the table are also included, for comparison, the experimentally determined yields of C_2 products, i.e. ethylene plus its probable hydrogenation product, ethane.

It is apparent that for both temperatures the calculated and experimental ethylene contents of the mixture issuing from the reaction vessel show the same general trends with propylene flow rates. The difference in the values of k_2/k_1 at the two temperatures corresponds to an activation energy for the attack of nitrogen atoms on propylene about 2 kcal, higher than the activation energy for

TRICK AND WINKLER: NITROGEN ATOM - PROPYLENE REACTION

Temp	$= 242^{\circ}C.,$	$k_2/k_1 = 0.75$	Ten	$np. = 96^{\circ}C.,$	$k_2/k_1 = 1.75$
$[C_3H_6]_0$	$[C_2H_4]_{calc.}$	$[C_2H_4]_{exp.}$ (as total C ₂)	$[C_{3}H_{6}]_{0}$	[C ₂ H ₄]cate.	$\begin{array}{c} [C_2H_4]_{exp.} \\ (as total C_2) \end{array}$
$\begin{array}{c} 2.12\\ 3.29\\ 3.46\\ 4.12\\ 5.08\\ 5.12\\ 6.55\\ 7.01\\ 9.32 \end{array}$	Incomplet nitrog 0.95 0.62 1.78 1.84 2.54 2.78 3.87	te removal of en atoms 0.33 0.69 1.62 0.90 2.50 2.95 4.60	$\begin{array}{r} 3.43 \\ 4.05 \\ 4.52 \\ 5.17 \\ 5.78 \\ 5.82 \\ 9.02 \end{array}$	$\begin{array}{c} 0.31 \\ 0.59 \\ 0.63 \\ 1.15 \\ 1.38 \\ 1.22 \\ 2.36 \end{array}$	$\begin{array}{c} 0.30\\ 0.86\\ 0.61\\ 1.24\\ 1.31\\ 1.35\\ 2.60\end{array}$

TABLE III COMPARISON OF CALCULATED AND EXPERIMENTAL YIELDS OF ETHYLENE

the corresponding reaction with ethylene. No reliable values for the individual activation energies are possible from the available data, owing to the complete consumption of the reactant that is present in smaller amount. However, the upper limit of the activation energy for the ethylene reaction is almost certainly less than 4 kcal. (14), and probably less than about 2 kcal. (8). Hence, the activation energy for the nitrogen atom - propylene reaction may be taken as less than 6 kcal., and probably less than 4 kcal.

Note added in proof (prompted by discussions at the meeting of the Faraday Society, Toronto, September 8 - 9, 1952). The results of this investigation, and of previous similar studies in this laboratory, have been interpreted by assuming atomic nitrogen to be the reactive species in active nitrogen. This view is based mainly on the approximate correspondence between the amount of nitrogen-containing products of reaction and the nitrogen atom content of the active nitrogen determined by Wrede gauge measurements, although the questionable reliability of atom concentrations inferred from such measurements is recognized. Should it be subsequently proven that other reactive species are involved, e. g. the N₃ molecule, it seems likely that the fundamental kinetic features could be represented with relatively little modification of the tentative schemes based on atomic nitrogen.

REFERENCES

BAWN, C. E. H. and DUNNING, W. J. Trans. Faraday Soc. 35:185. 1939.
 BAWN, C. E. H. and MILSTED, J. Trans. Faraday Soc. 35:889. 1939.
 BAWN, C. E. H. and TIPPER, C. F. H. Discussions Faraday Soc. 2:104. 1947.

BLADES, H. and WINKLER, C. A. Can. J. Chem. 29:1022. 1951.
 DOUGLAS, A. E. and HERZBERG, G. Can. J. Phys. 29:294. 1951.
 GEIB, K. H. and HARTECK, P. Ber. 66(B):1815. 1933.

- GEIB, K. H. and HARTECK, P. Ber. 00(B):1815. 1933.
 GREENBLATT, J. H. and WINKLER, C. A. Can. J. Research, B,27:721. 1949.
 GREENBLATT, J. H. and WINKLER, C. A. Can. J. Research, B,27:732. 1949.
 LAIDLER, K. J. and CASEY, E. J. J. Chem. Phys. 17:1087. 1949.
 LEROY, D. J. Can. J. Research, B,28:492. 1950.
 POOLE, H. G. Proc. Roy. Soc. (London), A,163:404. 1937.
 RABINOVITCH, B. S. DAVIES, S. G., and WINKLER, C. A. Can. J. Research, B,21:251. 1943.
- STEACIE, E. W. R. Atomic and free radical reactions. Reinhold Publishing Corporation, 13. New York. 1946.

14. VERSTEEG, J. and WINKLER, C. A. Unpublished results.