

Competition of Ethylene and Propane for
"Active" Nitrogen¹

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The extensive literature of "active" nitrogen chemistry does not appear to record any study of competition between organic substrates. This paper reports an investigation of consumption of hydrocarbon in the competition between an olefin, ethylene, and a paraffin, propane. Reaction probably went to completion under most, if not all, experimental conditions.² Consumption of hydrocarbon as a result of both primary attack by one or more components of "active" nitrogen and of secondary attack by reactive intermediates must be considered possible.

Experimental

Apparatus and methods are described more completely elsewhere,^{3,4}. Active nitrogen was generated by electrodeless glow discharge supported by 2450MHz microwaves at a total pressure of 311 Torr. Transport rates were 230cm. sec.⁻¹, 150 μ mole sec.⁻¹ and 1.3 \pm 0.2 μ mole sec.⁻¹ for linear flow, N₂ flow and N(⁴S) flow, respectively. The latter was measured by nitric oxide "emission" titration.⁵ Hydrocarbon substrate was introduced countercurrent³ into the active nitrogen stream at autogenous temperature (approx. 50°C) 20cm. (.087 sec.) downstream from the glow discharge. The gas stream passed through liquid nitrogen traps 50cm. (.22 sec.) downstream from the substrate inlet. Amounts of recovered reactants were determined by gas chromatography on silica gel.⁴ Relative activities of ¹⁴C-labeled compounds were determined⁴ by proportional counting of CO₂ obtained by combustion of the gas chromatographically purified compounds in O₂ over CuO at 450°. Propane and labeled ethylene were Matheson products. Cold ethylene was Phillips Research Grade.

Data

Table I summarizes percent consumption of ethylene consequent upon reaction of the pure substrate and three of its mixtures with propane with six different ratios of N(⁴S). Table II summarizes analogous data for propane. The data for mixtures given in the two Tables are derived from the same sets of experiments. Table III summarizes apparent relative specific rates of consumption, " $k_{C_2H_4}/k_{C_3H_8}$ ". These ratios were calculated by means of eq. 1, the expression which would be appropriate " $k_{C_2H_4}/k_{C_3H_8} = \log[(C_2H_4)_f/(C_2H_4)_t] / \log[(C_3H_8)_f/(C_3H_8)_t]$ " (1) if the relative rates of consumption depended entirely on the bimolecular reaction of each of the substrates with the same reagent. Table IV summarizes molar radioactivities of recovered reactants or product ethane relative to that of reactant ethylene for the reaction of equimolar mixtures of ¹⁴C-labeled ethylene and ordinary propane.

Table I

Percent Consumption of Ethylene

<u>(Total Hydrocarbon)</u> (N) ^a	Average Percent Consumption (C ₂ H ₄) ₀ /(C ₃ H ₈) ₀			
	Pure C ₂ H ₄ n ^b	3.0 n ^b	1.0 n ^b	0.33 n ^b
4	19 3	18 3	28* 10	-
2	24* 3	27 3	37* 10	51 6
1	39* 4	45 4	47 ^x 16	56 9
2/3	45 2	59 1	-	73° 2
1/2	78 ^x 3	87 3	93 10	90 7
1/6	93° 2	-	93 7	84 3

- a. Flow rate of N(⁴S) is $1.3 \pm 0.2 \mu$ mole sec.⁻¹ throughout.
 b. Number of independent determinations averaged to give the tabulated figure.

Table II

Percent Consumption of Propane

<u>(Total Hydrocarbon)</u> (N) ^a	Average Percent Consumption (C ₂ H ₄) ₀ /(C ₃ H ₈) ₀			
	Pure C ₃ H ₈ n ^b	3.0 n ^b	1.0 n ^b	0.33 n ^b
4	-	25 3	27* 10	-
2	29* 1	32 3	32* 10	22 6
1	35* 2	34 4	32 ^x 16	30 9
2/3	-	36° 1	-	32 2
1/2	41 ^x 2	39 3	39 10	37 7
1/6	48° 2	-	45 7	44 3

- a. Flow rate of N(⁴S) is $1.3 \pm 0.2 \mu$ mole sec.⁻¹ throughout.
 b. Number of independent determinations averaged to give the tabulated figure.

Table III

Apparent Relative Reactivities

<u>(Total Hydrocarbon)</u> (N)	"k _{C₂H₄} /k _{C₃H₈} "			
	Separate ^a	(C ₂ H ₄) ₀ /(C ₃ H ₈) ₀		
		3.0	1.0	0.33
		0.69	1.1	-
2	(0.30)	0.83	1.2	2.9
1	(1.2)	1.5	1.7	2.3
2/3	-	2.0	-	3.5
1/2	(2.9)	4.1	5.4	5.2
1/6	(6.0)	-	4.5	3.1

- a. Numbers in this column are calculated from the data for pure substrates. (Total Hydrocarbon) is taken arbitrarily as the concentration of one of the pure hydrocarbons. Values are based on data for identical concentrations of pure hydrocarbons.

Table IV

Relative Molar Activities of Recovered Reactants and Product Ethane^a

<u>(Total Hydrocarbon)</u> (N) ^d	Relative Molar Activity					
	C ₂ H ₄		C ₂ H ₆		C ₃ H ₈	
	n ^b	n ^b	n ^b	n ^b	n ^b	n ^b
2	0.98	7	-	-	0.01 ^c	1
1	0.98	4	-	-	-	-
1/2	-	-	0.8	1	0.01 ^c	1
1/6	0.89	2	0.5	1	0.01 ^c	1

- a. Compared to unreacted ethylene; hydrocarbon reactants equimolar.
 b. The number of independent experiments.
 c. Indistinguishable from the value found for unreacted propane.
 d. Flow rate of N(⁴S) was $1.3 \pm 0.2 \mu$ mole sec.⁻¹ throughout.

Discussion

The systematic variation of the ratio " $k_{C_2H_4}/k_{C_3H_8}$ " over the range of concentration parameters summarized in Table III demonstrates that relative consumption of competing hydrocarbons is not determined simply by the relative rates of attack of $N(^4S)$ (or any set of reactive species) on ethylene and propane since such determination would lead to constancy of the ratio. A similar conclusion can be drawn from the data of Tables I and II by comparison of the consumption of a given substrate at a fixed concentration upon reaction with a fixed proportion of $N(^4S)$ in the presence and absence of the competing substrate. Such matched points are designated in Tables I and II by identical superscripts. If the simple model of the competition from which eq. 1 is derived were correct, and keeping in mind the similar degrees of consumption of the two substrates, addition of the second substrate should always substantially suppress the consumption of the first and should have the largest effect when substrate is in excess over reagent. In fact, with (reactant hydrocarbon)/(N) ≥ 1 such suppression is absent or negligible. It becomes significant only when $N(^4S)$ is in excess. The complexity of the reaction is also indicated by the shallow dependence of percent consumption of pure hydrocarbon on the ratio, (pure hydrocarbon)/(N), particularly with propane for which a twelvefold decrease in the ratio is associated with increase in percent consumption by a factor of only 1.65. Such behaviour is consistent with destruction of the substrate by both attacking reagent and reactive intermediates arising from the primary attack if, as the proportion of $N(^4S)$ is raised, these intermediates are increasingly consumed by the reagent before they can attack the substrate. This feature is also present with ethylene but to a smaller extent.

Except with the largest excess of $N(^4S)$, the value of " $k_{C_2H_4}/k_{C_3H_8}$ " (Table III) increases with decrease in the ratio $(C_2H_4)_0/(C_3H_8)_0$ at constant values of (total hydrocarbon)/(N). This systematic change is consistent with occurrence of competition between the two substrates with respect to their destruction by reactive intermediates arising from primary attack of the reagent. More specifically, (cf. Tables I and II) ethylene appears to be more sensitive to consumption by intermediates arising from propane than vice versa. Presumably, the effect of attack by reactive intermediates can be reduced or eliminated by using sufficiently large excesses of $N(^4S)$ that the intermediates react with the latter rather than with hydrocarbon. This analysis suggests that the values of " $k_{C_2H_4}/k_{C_3H_8}$ " obtained with the largest excess of $N(^4S)$ most closely approximate the true value of this ratio for primary attack and indicates that this true value is at least 5. (See further discussion of the data at (hydrocarbon)/(N) = 1/6 below.)

The above discussion tacitly assumes that $N(^4S)$ is the only component of "active" nitrogen which is significantly involved. That this is so for ethylene is widely accepted. The work of Jones and Winkler⁶ suggests that it is probably also the case for propane. The latter study provides a value of $1.0 \times 10^6 M^{-1} sec^{-1}$ for the specific rate of reaction of C_3H_8 at $50^\circ C$. Since nitrogen atom concentrations were determined from HCN yields produced by reaction with ethylene, this constant should be adjusted downward 30 to 50%, e.g. to $7 \times 10^5 M^{-1} sec^{-1}$. Since the constant was apparently evaluated from experiments in which propane was in molar excess over propane it may also be significantly high because it does not correct for the consequences of attack by reactive intermediates arising from initial attack by $N(^4S)$. Herron has estimated from his elegant mass spectrometric study⁷ of the reaction of $N(^4S)$ with ethylene that the rate of primary attack in the (virtually temperature independent) reaction of $N(^4S)$ with ethylene is equal to or less than $7 \times 10^6 M^{-1} sec^{-1}$. A value of the ratio of specific rates of primary attack by $N(^4S)$ on ethylene and propane, respectively, in the vicinity of 10 is thus indicated by earlier work. Agreement with the present

result is well within the range of the mutual uncertainties. Herron's work further establishes that hydrogen atoms produced in the reaction of $N(^4S)$ with ethylene compete with the reagent for the substrate and, in fact, provides the model upon which interpretation of the present data is based.

The data of Table IV establish that even with a sixfold excess of $N(^4S)$, synthesis of propane⁴ in the reaction mixture at least in part from fragments originating in ethylene is not detectable. Production of ethylene either by degradation of propane or synthesis at least in part from fragments originating in propane occurs to a detectable extent with a sixfold excess of $N(^4S)$ and equal initial concentrations of the hydrocarbons. Presumably such processes are more important with propane in excess over ethylene. The values of " $k_{C_2H_4}/k_{C_3H_8}$ " obtained with a sixfold excess of $N(^4S)$ are, accordingly, reduced by such replacement of consumed ethylene, the reduction being greatest with excess propane. This effect results in reversal of the trend to higher values of " $k_{C_2H_4}/k_{C_3H_8}$ " with increasing excess of $N(^4S)$ which is apparent in the data of Table III. It can also account for the unusual sequence of values of this ratio with increasing proportion of propane observed with (hydrocarbon)/(N) = 6 and to a lesser extent when this ratio equals 2. The data of Table IV also establish that ethane is produced from both ethylene and propane.

Footnotes

1. Paper VI in the series, "Reactions of Active Nitrogen with Organic Substrates."
2. This statement is based on a study of the effect of trapping times on product yields in the reaction of "active" nitrogen with propylene by Dr. Y. Titani in these laboratories. Cf. N. N. Lichtin, Int. J. Radiation Biol., in press.
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5. P. Harteck, G. G. Mannella and R. R. Reeves, J. Chem. Phys., 29, 608 (1958).
6. W. E. Jones and C. A. Winkler, Can. J. Chem., 42, 1948 (1964).
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