U	OMPLEXATION V	JUNSTANTS OF	COPPER WITH ORUS	S-LINKED AN	D LINEAR OARBOA.	ILIC ACIDS
Polymer acid	Concn. of NaNOs, J	M log Bav	$B_2$	$b_1/b_2$	$K_2$	K2'
PAA (0.01 N)	0.	-1.19	4.2 $\times 10^{-3}$	2.1	$9.1 \times 10^9$	
	0.2	-1.17	$4.6 \times 10^{-3}$	0.76	$3.0 \times 10^{7}$	
	2	-0.99	$1.05 \times 10^{-2}$	0.33	$9.6  imes 10^6$	
XE 89	0.2	-1.67	$4.57 \times 10^{-4}$	1.2	$9.55  imes 10^7$	
	2	-1.70	$3.98 imes10^{-4}$	1.4	$1.73 imes10^6$	
DVB-1	0	-2.35	$2.00 imes10^{-5}$	0.31	$3.02 imes10^{10}$	$1.4 \times 10^{7}$
	0.2	-2.40	$1.59 imes10^{-5}$	0.77	$2.51 imes10^7$	$3.2 imes10^{5}$
	2	-2.70	$3.98 imes10^{-6}$	13	$2.51 imes10^5$	$9.3 imes10^4$
DVB-9	0	-2.70	$3.98  imes 10^{-6}$	0.31	$1.26 \times 10^{11}$	$5.1 imes10^7$
	0.2	-2.89	$1.66 \times 10^{-6}$	2.7	$2.88 imes10^7$	$8.3 imes10^{5}$
	<b>2</b>	-3.06	$6.03 \times 10^{-7}$	31	$5.75 imes10^{5}$	$1.0 imes10^{5}$

TABLE II

COMPLEXATION CONSTANTS OF COPPER WITH CROSS-LINKED AND LINEAR CARBOXYLIC ACIDS

Observation of the values for the complexation constants  $B_2$  in column four shows the following trends: in all resin systems the complexation is considerably weaker than in the linear case; this is again undoubtedly due to the greater rigidity of the cross-linked chains. This view is borne out by comparison between the values found for the DVB-9 and DVB-1 resins; the more highly cross-linked and therefore "stiffer" DVB-9 system shows the smaller constants. Also, both methacrylic systems show lower constants than the acrylic resin XE 89, which can be considered more flexible.

The variation of  $B_2$  with salt concentration is again slight; it is, however, in opposite directions in the case of the linear and cross-linked materials. Examination of column five makes the reason for this apparent. While the spreading factor  $b_1/b_2$  increases with increasing salt concentration for crosslinked systems, it decreases for linear PAA. This shows that while  $b_1$ , the constant for the first step, is quite unaffected by salt concentration changes, the second constant  $b_2$  decreases considerably for cross-linked systems but increases for linear systems. It can be surmised that the latter is due to the chain contraction which brings successive complexing groups into closer proximity with one another and which outweighs a simple activity effect which alone is operative in the cross-linked case.

The discrepancy between the values of  $K_2$ , obtained from  $B_2$  by the use of equation 6 of reference 2, and of  $K_2'$ , obtained directly from copper analyses, is considerable in low salt concentrations. Part of this discrepancy undoubtedly is due to the lack of significance of the constant  $K_2$  as explained in reference 2, and part of it reflects the lack of validity of the assumption that the Donnan equilibrium is swamped inside the resin particle, as was pointed out above. The agreement at high salt concentrations is satisfactory, as expected.

This investigation was supported in part by a research grant, RG 2934(C2), from the Division of Research Grants of the National Institutes of Health, Public Health Service. We also wish to express our gratitude to the Rohm and Haas Company which provided us with samples of the polyacrylic acid resin used in this investigation.

# THE REACTION OF ACTIVE NITROGEN WITH NEOPENTANE<sup>1</sup>

By M. ONYSZCHUK<sup>2</sup> AND C. A. WINKLER

Contribution from the Physical Ch.mistry Laboratory, McGill University, Montreal, Quebec, Canada

### Received October 14, 1954

Besides large quantities of hydrogen cyanide, small amounts of ethylene, acetylene, propylene and propane were recovered from the reaction of active nitrogen with neopentane. Second-order rate constants were calculated for the reaction at eight temperatures between -40 and  $350^{\circ}$ . An Arrhenius plot showed a pronounced curvature with definite indication of two activation energies; the average values of these were  $2.0 \pm 0.5$  and  $7.1 \pm 0.6$  kcal./mole in the range -40 to  $115^{\circ}$  and 150 to  $350^{\circ}$ , respectively, with corresponding steric factors of about  $10^{-3}$  and  $10^{-3}$ . This observation was interpreted to indicate a composite reaction due to alternative modes of active nitrogen attack on the neopentane molecule, to the presence of two reactive species in the active nitrogen stream, or possibly to the influence of simultaneous hydrogen atom reactions.

Activation energies have been estimated for the reactions of active nitrogen with ethane,<sup>3</sup> propane,<sup>4</sup> and isobutane,<sup>5</sup> *i.e.*, for reactions involving hydrocarbons containing bonds between a primary carbon

- (1) With financial assistance from the National Research Council of Canada.
- (2) Holder of National Research Council Studentships 1952-1954.
- (3) H. Blades and C. A. Winkler, Can. J. Chem., 29, 1022 (1951).
  (4) M. O. Onyszchuk, L. Breitman and C. A. Winkler, *ibid.*, 32, 351 (1954).
  - (5) R. A. Back and C. A. Winkler, ibid., 32, 718 (1954).

atom and a primary, secondary and tertiary carbon atom, respectively. To examine further the behavior of various carbon-carbon bonds in these reactions, it was of interest to investigate the active nitrogen-neopentane reaction in which bonds between a quaternary and primary carbon atoms would be concerned.

### Experimental

The apparatus and analytical methods used in this investigation have been described in previous papers from this Laboratory. The molecular nitrogen flow rate was maintained constant at  $5.83 \times 10^{-5}$  mole per sec., which gave a pressure of 1.34 mm. of mercury in the flow system, while neopentane flow rates were varied from about  $5 \times 10^{-7}$  to  $1.5 \times 10^{-5}$  mole per sec. The flow rate of active nitrogen, produced by a condensed discharge, remained constant during the course of a series of experiments at any given temperature, and changed only after the reaction vessel was cleaned with chromic acid and repoisoned with metaphosphoric acid.

Two grades of neopentane, obtained from Phillips Petroleum Company, were used; one was "pure grade" with a minimum purity of 99 mole %, the other was "research grade" with a certified purity of 99.87 mole % (the most probable impurity was isobutane). Both grades of neopentane were used after the usual procedure of degassing and a simple trap-to-trap distillation.

In one series of experiments with 99% neopentane complete analysis of reaction products was made.<sup>6</sup> Three or more experiments were conducted at each of seven temperatures in the range 55 to 250°. Temperatures were attained and manually controlled to within  $\pm 5^{\circ}$  by an electrically heated furnace, and were measured with a copper-constantan thermocouple situated at the outlet of the hydrocarbon jet in the center of the reaction vessel. Three experiments were also made at a reaction flame temperature of  $-40^{\circ}$ , during which the walls of the reaction vessel were kept at Dry Ice temperature.

After the reaction vessel was cleaned and repoisoned so that a different active nitrogen concentration prevailed,<sup>7</sup> some check experiments were made with neopentane of 99.87% purity, but without complete product analysis. The results obtained for analyses of hydrogen cyanide and total  $C_2 + C_3$  hydrocarbons confirmed the essential characteristics of the reaction established in the preceding series of experiments, and since the data for the 99% neopentane are more complete, only the results of these experiments are reported in detail.

### Results

Hydrogen cyanide was the principal product of the active nitrogen-neopentane reaction and the only one that contained nitrogen. It was recov-ered in yields of 92-99% of the neopentane con-sumed by reaction at 250°, while the percentage neopentane converted to products varied from 5.8% at the highest to 33.5% at the lowest neopentane flow rate used. From Fig. 1, which illustrates the yields of products from experiments with 99% neopentane, it is evident that complete consumption of active nitrogen, indicated by constant hydrogen cyanide production, was attained only at  $250^{\circ}$  for neopentane flow rates greater than about  $6 \times 10^{-6}$  mole per sec. The maximum yield of hydrogen cyanide,  $4.6 \times 10^{-6}$  mole per sec., presumably corresponds to the concentration of active nitrogen available for reaction with neopentane at any temperature. For reaction temperatures less than 250°, the observed gradual increase in hydrogen cyanide formation with increasing neopentane flow rate represents a progressive depletion in concentration of active nitrogen.

Secondary products, recovered in measurable amounts at all neopentane flow rates, were ethylene, acetylene, propylene and propane. Ethane was also detected but only in trace quantities. The variations in yields of secondary products with neopentane flow rate, shown in Fig. 1, indicate a general behavior similar to that observed in the propane reaction.<sup>4</sup>

Since the sum of secondary products from the neopentane reaction, as in the propane system, ac-

(6) We are grateful to Dr. H. I. Schiff of this department for mass spectrometer analyses.



counted for less than 10% of hydrocarbon consumption, the neopentane that reacted was almost completely degraded to hydrogen cyanide. This suggests that the mechanism of the neopentane reaction probably consists of an initial step which is rate-controlling followed by a series of rapid consecutive reactions which produce hydrogen cyanide. If the primary attack of active nitrogen on neopentane is considered to be rate-determining, the over-all reaction can be shown to obey the second order rate law.<sup>3</sup> Streamline and turbulent flow conditions in the spherical reaction vessel were assumed as alternatives for the calculation of second-order rate constants, with the results summarized in Table I, together with those derived from experiments with 99.87% neopentane.

TABLE I

Second-order	RATE (	Constants	AT	VARIOUS	TEMPERA-
TURES FOR THE	ACTIVE	NITROGEN-	-Neo	OPENTANE	REACTION
		Streamling #	· · · · ·	The sheet	1 d

Temp., °C.	Streamline flow $k \times 10^{-4}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	Turbulent flow $k \times 10^{-6}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
	99% Neopentane	
$-40 \pm 5$	0.37	1.0
$55 \pm 5$	1.5	4.7
$114 \pm 5$	2.5	8.1
$140 \pm 3$	3.3	12
$153 \pm 3$	3.8	15
$173 \pm 5$	7.2	40
$250 \pm 5$	20	110
	99.87% Neopentane	
$-35 \pm 5$	0.67	1.8
$47 \pm 3$	1.6	4.7
$150 \pm 5$	6.4	23
$245 \pm 5$	14	83
$360 \pm 5$	43	410

<sup>(7)</sup> G. S. Trick and C. A. Winkler, Can. J. Chem., 30, 915 (1952).

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Although values for turbulent flow were consistently higher than those for streamline flow, an Arrhenius plot, shown in Fig. 2, clearly indicates



a parallel behavior for both sets of data. Since reproducible results were obtained with both grades of neopentane in spite of a difference in experimental conditions, it is concluded that the curvature in the activation energy plot is a genuine effect. From the slopes of the two nearly linear portions of the plots, the activation energies shown in Table II were estimated. Actual flow conditions were probably somewhere between the two extremes assumed and the individual values of the activation energies may be taken to represent the limits within which the true values probably lie. Frequency factors, A, in the Arrhenius equation, calculated for the reaction at 55 and 250°, are recorded in Table III, together with steric factors, P, calculated from collision theory by using 3.0 and 6.0 Å. for the collision diameters of atomic nitrogen<sup>8</sup> and neopentane,<sup>9</sup> respectively.

#### TABLE II

ACTIVATION ENERGIES FOR THE ACTIVE NITROGEN-NEO-PENTANE REACTION

Temp. range, °C.	Streamline flow	E, kcal./mc Turbulent flow	le Av.
-40 to 115	2.0	2.0	$2.0 \pm 0.5$
150 to 350	6.5	7.7	$7.1 \pm 0.6$

(8) J. H. Greenblatt and C. A. Winkler, Can. J. Research, **B27**, 732 (1949).

### Discussion

The following table indicates the relative position of neopentane, with its bonds between quaternary and primary carbon atoms, in a series of hydrocarbons for which activation energies and steric factors have now been estimated for the reactions with active nitrogen

Hydrocarbon	E, kcal./mole	Р
Methane	11	$5 imes 10^{-3}$
(Neopentane)	7.1	$10^{-4}$ to $10^{-2}$
Ethane	7.0	10 <sup>-s</sup> to 10 <sup>-1</sup>
Propane	5.6	$10^{-4}$ to $10^{-2}$
n-Butane	3.6	$4 \times 10^{-4}$
Isobutane	3.1	$4 \times 10^{-4}$
(Neopentane)	2.0	$10^{-6}$ to $10^{-5}$

It is possible that suitable extension of experimental conditions might show some of the reactions other than that with neopentane to be characterized by two activation energies. Only in the study of the ethane reaction<sup>3</sup> were rate constants determined at several temperatures, and a linear plot was obtained over the range 100 to 300°. However, experiments were not extended to lower temperatures, where the curvature in the activation energy plot for neopentane becomes apparent.

The obvious conclusion to be drawn from the detection of two activation energies for the neopentane reaction is that the over-all reaction is composite. This might be attributed to different modes of active nitrogen attack on the neopentane molecule, to the presence of two reactive species in the active nitrogen stream, or possibly to the influence of hydrogen atom reactions which produce radicals that react rapidly with active nitrogen. It is improbable that surface effects at low temperatures would give rise to the non-linear Arrhenius plot. If surface were responsible, erratic yields of hydrogen cyanide might be expected for experiments at low temperatures, since some condensation and slight polymerization of hydrogen cyanide on the walls of the reaction vessel were observed after several experiments at  $-40^{\circ}$ . No such behavior was apparent at higher reaction temperatures, yet reproducible results were obtained at any given temperature.

Active nitrogen reaction with neopentane in two different ways immediately suggests that one activation energy corresponds to attack at a methyl group, the other to attack at the central carbon The smaller steric factor, about  $5 \times 10^{-6}$ , atom. would be reasonably assigned to the latter. However, this is, in turn, associated with the smaller activation energy of 2 kcal. per mole. It is difficult to conceive of a mode of attack at the central carbon atom that would have an activation energy lower than reaction at the primary carbon atoms, and at the same time satisfactorily account for the relatively small change in composition of secondary products with temperature. In fact, it is difficult to understand how the focus of reaction at the quaternary carbon atom could give rise to the products isolated at any temperature. However, the unusual behavior of neopentane in other reactions makes it difficult to rule out different modes of active nitrogen attack. For example, compared with

<sup>(9)</sup> A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, J. Chem. Phys., 19, 163 (1951).

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TABLE	III
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### KINETIC CONSTANTS FOR THE ACTIVE NITROGEN-NEOPENTANE REACTION

condition assumed	Temp., °C.	k	$\overset{A}{1. \text{ mole}^{-1} \text{ sec.}^{-1}}$	Z	Р	E, kcal./mole
Streamline	55	$1.5 imes10^4$	$3.2 imes10^5$	$3.0  imes 10^{11}$	$1.1 \times 10^{-6}$	2.0
	250	$2.0 imes10^{5}$	$1.0 imes10^8$	$3.7 imes10^{11}$	$2.7 imes10^{-4}$	6.5
Turbulent	55	$4.7 imes10^{5}$	$1.0 imes10^7$	$3.0  imes 10^{11}$	$3.3 imes10^{-s}$	2.0
	<b>250</b>	$1.1 imes10^7$	$1.8 imes10^{10}$	$3.7 imes10^{11}$	$4.9  imes 10^{-2}$	7.7

the lower paraffins neopentane is surprisingly inert to mercury photosensitization. The low quantum vield found by Darwent and Steacie<sup>10</sup> was attributed to the predominant role of symmetry of the neopentane molecule in this reaction. In this way neopentane resembles methane rather than ethane which has carbon-hydrogen bonds of strength similar to those in neopentane. On the other hand, neopentane behaves like ethane in reaction with atomic hydrogen produced by a discharge, since both reactions proceed at approximately the same rate, with activation energies of about 9 kcal. per mole, assuming a steric factor of 0.1.<sup>11</sup> Unlike the results for other paraffins, the most remarkable feature of the atomic hydrogen-neopentane reaction at 24° is the comparatively high yield of ethane and its increase with increasing hydrogen atom concentration.

An alternative interpretation of the two activation energies in the active nitrogen-neopentane reaction may involve the presence of two reactive species in active nitrogen, which perhaps react with neopentane at different rates. Since no apparent differences were observed in the composition of secondary products recovered in the two activation energy regions, both species would probably have to react by similar, though perhaps not identical, mechanisms. It is generally agreed that nitrogen atoms are produced in the discharge tube, and it is

(10) B. deB. Darwent and E. W. R. Steacie, Can. J. Research, **B27**, 181 (1949).

(11) W. R. Trost and E. W. R. Steacie, J. Chem. Phys., 16, 361 (1948).

likely that they constitute a chemically reactive species. It would seem, therefore, that the type of reaction mechanism involved might be analogous to those previously outlined with the assumption of atomic nitrogen as the only active species.<sup>4,5</sup> Briefly, this would involve for neopentane the following main reactions

CH₃

$$\begin{array}{ccc} CH_{3}-\overset{}{C}-CH_{3}+N \longrightarrow CH_{3}-\overset{}{C}-CH_{3}+HCN+H_{2}\\ CH_{3} & CH_{3} & (1) \end{array}$$

$$CH_{3}-\dot{C}-CH_{3} + N \longrightarrow CH_{3}-\dot{C}-CH_{3} + HCN + H$$

$$CH_{3}-\dot{C}-CH_{3} + HCN + H$$

$$(2)$$

$$CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_3$$
 (3)

$$CH_3CH = CH_2 + N \longrightarrow CH_2 = CH_2 + HCN + H$$
 (4)

 $CH_{3}CH = CH_{2} + N \longrightarrow$ 

$$CH \equiv CH + HCN + H_2 + H \quad (5)$$

Reactions 4 and 5 might be followed by further reactions of nitrogen atoms with ethylene<sup>12</sup> and acetylene.<sup>13</sup> If reaction 1 is the rate-controlling step, while subsequent reactions are very rapid, this mechanism predicts extensive conversion of neopentane to hydrogen cyanide and relatively small recovery of secondary unsaturated products, in agreement with the kinetic behavior shown in Fig. 1.

(12) J. Versteeg and C. A. Winkler, Can. J. Chem., **31**, 1 (1953).
(13) J. Versteeg and C. A. Winkler, *ibid.*, **31**, 129 (1953).

## THE REACTION OF ACTIVE NITROGEN WITH AMMONIA<sup>1</sup>

# By G. R. FREEMAN<sup>2</sup> AND C. A. WINKLER

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec<sup>1</sup>

### Received October 14, 1954

Active nitrogen has been found to destroy ammonia to an optimal extent which is independent of temperature over a wide range, and which represents approximately one-sixth of the total activity in the nitrogen, determined from its ability to form hydrogen cyanide with ethylene. It is concluded that there are at least two chemically reactive species in active nitrogen.

The reactions of active nitrogen with a number of hydrocarbons (and alkyl halides) have been studied in this Laboratory, and tentatively interpreted by assuming atomic nitrogen to be the only reactive species in the active nitrogen. However, a recent investigation of the analogous reaction with

(1) With financial assistance from the National Research Council of Canada.

(2) Holder of a Fellowship under the National Research Council of Canada.

neopentane<sup>8</sup> has indicated that more than one reactive species may exist in active nitrogen. The present study of the ammonia-active nitrogen reaction appears to provide unambiguous information on this point. Previous studies by Willey and Rideal<sup>4</sup> indicated that ammonia was readily decomposed

(3) M. Onyszchuk and C. A. Winkler, J. Phys. Chem., 59, 368 (1955).

(4) (a) E. J. B. Willey and E. K. Rideal, J. Chem. Soc., 669 (1927);
(b) J. K. Dixon and W. Steiner, Z. physik. Chem., B17, 327 (1932).