



The Mercury Photosensitized Hydrogenation of Ethylene, Propylene, and n Butylene

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Transition in Nickel Nitrate Hexammoniate

The low temperature crystal structure of nickel nitrate hexammoniate has been investigated by Yü,1 who found evidences of very high thermal agitation of the nitrate groups in the crystal. We have measured the heat capacity curve for this substance from 54°K to 300°K, using a modified Nernst vacuum calorimeter. The data, shown in Fig. 1, indicate the existence of two regions of high energy absorption, one a typical lambda-type transition extending from 173°K to 247°K, with a maximum value at 243°K, and the other a region of anomalous energy absorption below 85°K.

The lambda transition can be supercooled to liquid-air temperatures and held there indefinitely without transforming; the rate of transformation becomes appreciable only upon warming to about 200°K. Cooling-curve measurements indicate a hysteresis effect of several degrees. In one cooling experiment, the minimum cooling rate occurred at 239°K.

The height of the lambda-peak at 243°K is not determinable; our highest C_p measurement in this region was 1270 calories/mole/degree, certainly a lower limit. The total heat absorption in excess of that represented by the "normal" heat capacity curve was obtained by "heat of transition" measurements extending from 227-247°K, thus including the area which could not be integrated graphically. The excess heat effect (above the "normal" curve from 173-247°K) is 1818 calories/mole. The corresponding entropy is 7.65 ± 0.5 E.U.

This high entropy of transition seems to invalidate any explanation involving rotation of only the nitrate groups in the crystal lattice. The assumption that both the ammonia and nitrate groups are executing rotational oscillations gives fair agreement with the experimental entropy, and with the value of C_p just above the transition. This assumption is in accordance with the theory of Frenkel,² and that of Kirkwood,3 which assume that the active groups are librating both below and above the transition, and that the transition is simply a process of disorientation, or the disordering of these librations with respect to the



FIG. 1. Heat capacity in calories per degree per mole of nickel nitrate hexammoniate.

crystal axes. A more precise check of the assumption could probably be made from an investigation of C_{v} values in the transition region.⁴ If the ammonia groups are librating, as proposed, the prsence of nitrate or similar groups would seem to be required, since cooling-curve measurements on nickel chloride hexammoniate5 show no indication of a transition. We are investigating ammonium chlorostannate and other substances of similar crystal structure to the nickel hexammoniates, in order to establish more definitely the conditions for this phenomenon.

The region of anomalous energy absorption below 85°K is of much smaller magnitude, the C_p values being about five percent high. The dotted line in Fig. 1 shows the results of measurements made on a sample which had been partially supercooled through the 243° transition. The presence of the form stable above 243° almost completely eliminates the high energy absorption below 85°. Measurements at temperatures considerably below 54°K will be necessary for a full description of the phenomenon.

A detailed report of the work will be published later. This investigation has been supported by a grant from the University of Missouri Research Council.

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The Mercury Photosensitized Hydrogenation of Ethylene, Propylene, and n-Butylene

A convenient method of preparing a free aliphatic radical is by the addition of a hydrogen atom to the corresponding olefine; if the hydrogen atoms are produced by mercury photosensitization their concentration will be low compared with the radical concentration, and subsequent reactions of the radicals with each other may be studied. Thus Taylor and Jungers¹ reported that butane was the predominant product from the mercury photosensitized hydrogenation of ethylene.

In an apparatus similar to that of Taylor and Jungers we have compared the reactions of ethyl, propyl, and butyl radicals formed in a similar fashion. In each case olefine at about forty millimeters pressure, mixed with a sixfold excess of hydrogen, was illuminated at room temperature in the presence of mercury vapor with 2536.7A radiation. The analytical method employed was a suitable adaptation

TABLE I.

	PERCENTAGE OF OLEFINE TO SATURATED PRODUCTS						
OLEFINE USED	CH4	C2H6	C ₃ H ₈	C4H10	C5H12	C6H14	C8H18
C2H4 C3H6 C4H8	2 2 3	14 1 1	$\frac{\overline{26}}{1}$	84 5 29	~_2	<u>-</u> -	 66

of that previously described.2 The results are given in Table I as the means of two concordant experiments with each olefine. In some of the experiments a trap cooled to -78° was used to decrease if possible the amount of lower hydrocarbon products formed, by preventing more extensive secondary reactions of higher hydrocarbons with hydrogen atoms.

There is a significantly greater formation of propane and butane from propylene and butylene than of ethane from ethylene. A possible explanation may be that addition of a hydrogen atom to propylene and n-butylene may form the isopropyl and isobutyl radicals as well as the normal radicals. Our earlier work with mercury diethyl indicates that the disproportionation reaction $2C_nH_{2n+1} = C_nH_{2n+2}$ $+C_nH_{2n}$ is not important with the normal radicals, C_2H_{5} . The reaction may become of greater importance when isoradicals are involved. It is of interest in this connection to compare the observation of Norrish3 that considerable amounts of propane and propylene are formed from the photolysis of di-isopropyl ketone, while neither of these products is obtained from di-n-propyl ketone.

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Frick Chemical Laboratory, Princeton University, Princeton, New Jersey, May 10, 1940.

¹ H. S. Taylor and J. C. Jungers, J. Chem. Phys. 6, 325 (1938).
 ² W. J. Moore, Jr., and H. S. Taylor, J. Chem. Phys. 8, 396 (1940).
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The Thermodynamic Properties of the PN Molecule*

In 1938 Moureu and Wetroff¹ showed that equimolecular quantities of phosphorus and nitrogen, when heated together, form a compound $(PN)_x$. In a more recent paper Moureu and his co-workers² show the existence of an equilibrium between (PN)_x and PN, and also one between PN and P2+N2. In view of their results, we thought that it might be of interest to calculate from spectroscopic data the thermodynamic properties of a perfect gas composed of PN molecules, and the equilibrium constant for the gaseous reaction

$$P_2 + N_2 = 2PN. \tag{1}$$

By combining the values for the equilibrium constant of reaction (1) with the values of the equilibrium constant for the reaction

$$\mathbf{P}_4 = 2\mathbf{P}_2 \tag{2}$$

given by Dushman,3 the equilibrium constant for

$$P_4 + 2N_2 = 4PN \tag{3}$$

can be calculated.

The results of these calculations are listed in Tables I and II.

In the calculation of the thermodynamic functions, the total partition function Q is given by

 $Q = Q_{\text{trans}} \cdot Q_{\text{internal}} \cdot Q_{\text{correction}}$

 Q_{trans} has been calculated by the usual method assuming a perfect gas. Qinternal assumes an harmonic oscillator

TABLE I. The thermodynamic functions of the PN molecule. (One mole of the perfect gas at one atmosphere.)

Темр. °К	$-(F-F_0)$ CAL.	(H-H ₀) CAL.	S CAL./DEGREE	<i>C</i> _p cal./degree
100.0 298.1	3588.0 12959.8	694.6 2079.1	42.824 50.448	6.9544 7.0973
750.0 1000.0	23333.0 37538.7 52209.0	5546.6 7633.8	54.235 57.450 59.842	8.1759 8.4774

TABLE II.	The e	quilibrium	constant.	for	$P_2 +$	N_2	=2PN.
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Темр. °С	$K_{pe} + \Delta E_0/RT$	$e^{-\Delta E_0/RT}$	Kp
800	6.09	7.87	47.9
900	5.94	6.58	39.1
1000	5.82	5.68	33.1

and a rigid rotator. From the value of Q_{correction} due to anharmonicity in the oscillation and to the lack of rigidity in the rotation given by Mayer and Mayer,⁴ we have calculated the following formulae for the corrections in the thermodynamic functions. The symbols used are defined in reference (4).

$$\begin{aligned} F_{\text{correction}} &= -\frac{RT}{u} \bigg[8\gamma + \frac{\delta u}{e^u - 1} + \frac{2xu^2}{(e^u - 1)^2} \bigg], \\ S_{\text{correction}} &= R \bigg[\frac{16\gamma}{u} + \frac{\delta}{e^u - 1} + \frac{\delta ue^u}{(e^u - 1)^2} + \frac{4xu^2e^u}{(e^u - 1)^3} \bigg], \\ H_{\text{correction}} &= RT \bigg[\frac{8\gamma}{u} + \frac{u(\delta e^u - 2x)}{(e^u - 1)^2} + \frac{4xu^2e^u}{(e^u - 1)^3} \bigg], \\ C_{\text{correction}} &= R \bigg[\frac{16\gamma}{u} - \frac{u^2 \delta e^u}{(e^u - 1)^2} + \frac{2u^2 e^u (\delta e^u - 4x - 2ux)}{(e^u - 1)^3} + \frac{12xu^3 e^{2u}}{(e^u - 1)^4} \bigg]. \end{aligned}$$

The molecular constants which we have used were taken from the literature.⁵ From the given values of the heats of dissociation, ΔE_0 for reaction (1) is calculated to be -0.2electron volt.

According to the work of Moureu and his co-workers,² PN at 800°C is almost completely dissociated into P2 and N2. The difference between this work and the values we have obtained may be attributed to the fact that the E_0 for PN has been determined by an extrapolation method, 5c and is probably an upper limit. A change in E_0 for PN of only a few tenths of an electron volt would have the effect of lowering the calculated value of K_p .

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Havemeyer Laboratories, Columbia University, New York, New York, May 13, 1940.

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