

1–4 Addition and Subtraction Reactions in Hydrocarbon Chemistry

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LETTERS TO THE EDITOR

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Spectroscopic Evidence for the Molecule PN

In a discharge through air in a tube which previously had been used with phosphorus we found a rather extensive system of simple diatomic bands in the region 2400–2900 Å which had not been recorded before. Further experiments showed that these new bands do not occur in a similar discharge through air or nitrogen *without* the presence of phosphorus. On the other hand they have never been observed in discharges through phosphorus vapor alone. The bands do however occur strongly in a discharge through a *mixture* of pure nitrogen and pure phosphorus vapor (at the same time strong clean-up occurs). We therefore conclude that the band system is due to the diatomic molecule PN. This is confirmed by a closer analysis of the band system (see below).

A search through the literature showed that the only well-known compound of phosphorus and nitrogen is P_3N_5 , discovered by Stock. In addition Moldenhauer¹ found several years ago that in a discharge through nitrogen and phosphorus a yellow powder is formed which contains equal amounts of phosphorus and nitrogen and which is remarkably stable. The free molecule PN in the vapor phase has not been observed up until now. The above experiments show that this molecule at least temporarily exists in gas discharges through a mixture of N_2 and P_4 .

We have so far measured the heads of 24 bands. These are represented rather accurately by the formula

$$\nu = 39,699.3 + (1094.75\nu' - 7.25\nu'^2) - (1329.38\nu'' - 6.98\nu''^2).$$

The fine structure of the bands is fairly well resolved on our plates (second order of 3 m grating). Each band con-

sists of one P , one Q and one R branch, thus the system is a ${}^1\Pi \rightarrow {}^1\Sigma$ transition (most probably the lower state is ${}^1\Sigma$). Therefore the remote possibility that the system is due to PO or CP, which might have been present as impurities, is excluded, because these can only have doublet (or quartet) terms. A preliminary rotational analysis gave the constants:

$$B_0'' = 0.78 \text{ cm}^{-1}, B_0' = 0.73 \text{ cm}^{-1}; r_0'' = 1.49 \text{ Å}, r_0' = 1.54 \text{ Å}.$$

These, as well as the vibrational constants (see the above formula) are similar to those for the corresponding systems of CS and SiO, as is to be expected. This is a further argument for PN as carrier of the band system.

It seems probable that the lower electronic level ${}^1\Sigma$ of the bands is the ground state of the molecule. The energy of dissociation of this state comes out by linear extrapolation to be 7.8 volts. This of course is to be regarded as an upper limit.

A full report of this work will appear shortly elsewhere. A further investigation of this molecule, both in emission and absorption, seems promising especially with respect to a comparison with N_2 and P_2 .

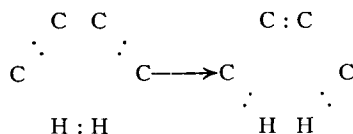
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August 19, 1933.

¹ W. Moldenhauer, Chem. Ber. 59, 926 (1926).

1-4 Addition and Subtraction Reactions in Hydrocarbon Chemistry¹

Eyring, Sherman, and Kimball² have treated 1-4 addition to conjugate double bonds by means of the model



where each dot represents an electron considered in the calculations. Using 74.5, 92, and 102.4 kcal. for the

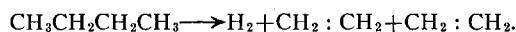
strengths of the C–C, C–H, and H–H bonds, they find an activation energy of 64 kcal. for the addition of hydrogen to conjugate double bonds. These bond strengths, however, give a heat of reaction of only 7.1 kcal., whereas heats of combustion require 32 kcal. This difference must

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² Eyring, Sherman and Kimball, J. Chem. Phys. 1, 586 (1933).

be made up mainly by decreasing the strength of C—C, which denotes actually the difference between C=C and C—C. The calculated heat of activation then will be somewhat lower, probably about 50 kcal. Sherman and Eyring,³ using a more suitable value for C=C, previously calculated an activation energy of 51.5 kcal. for the hydrogenation of ethylene. Here again the reaction is approximately 30 kcal. exothermic. The theoretical activation energy for either 1-2 or 1-4 dehydrogenation is thus 80 kcal.; the experimental value in the former case is 70 kcal., and a similar figure seems reasonable for the 1-4 reaction.

There is also a second possible type of 1-4 dehydrogenation:⁴



This type actually corresponds somewhat more closely to the six-electron model than does the production of butadiene from butylene. It is approximately 20 kcal. more endothermic, however, since it takes more energy to break C—C than it does to reduce C=C to C—C. The difference in activation energy will be considerably less than 20 kcal.; accurate predictions are impossible, but it appears worth while to look for this type of decomposition of hydrocarbons with a straight chain of at least four carbon atoms. By analogy with the 1-2 case, we shall expect to find 1-4 loss of methane, ethane, etc., and also, when the parent hydrocarbon is large enough.

The recent work of Frey and Hepp⁵ may be interpreted as showing that this type of reaction occurs. For *n*-butane itself the evidence is somewhat conflicting; 1-4 dehydrogenation may constitute up to 5 percent of the primary reaction. For *n*-pentane the data may be interpreted as indicating the following primary products.

	Percent		Percent
$\text{H}_2 + \text{C}_6\text{H}_{10} \dots\dots$	5.2	$\text{H}_2 + \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 \dots\dots$	18.5
$\text{CH}_4 + \text{C}_4\text{H}_8 \dots\dots$	30.9	$\text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 \dots\dots$	12.2
$\text{C}_2\text{H}_6 + \text{C}_3\text{H}_6 \dots\dots$	31.5		
$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_4 \dots\dots$	1.7		
	69.3		30.7

For *n*-hexane, 60 percent of the reaction seems to go by way of 1-4 unsaturation, and only 40 percent by 1-2. For 2-methylbutane and 2,3-dimethylbutane, 20 percent and 12 percent, respectively, of the total reaction involves

1-4 unsaturation. These results have been interpreted by Frey and Hepp, and by Rice,⁶ in terms of Rice's free radical mechanism. A detailed analysis shows that the free radical theory and the present unsaturation theory predict the same products in approximately the same yields. For very long chains it would be necessary to postulate 1-6, 1-8, etc., unsaturation, with resulting scission into four, five, or more primary products, to match exactly the free radical predictions; there is no experimental evidence on this point. The free radical mechanism does predict a decrease in the mean molecular weight of the primary products as the pressure is lowered. On the unsaturation theory such a decrease should not occur in the region where the reaction rate is strictly first order. No existing data even approach being good enough to make this test.

There is little doubt that free radicals are formed from metal alkyls, and in a few other cases where there are unusually weak bonds, but it appears possible to give a nearly complete account of the decomposition reactions of organic chemistry in terms of 1-1, 1-2, and 1-4 unsaturation. It is hoped to discuss this subject in more detail later. For the present, it is sufficient to mention a few further examples of 1-4 unsaturation: the formation of ethylene and butadiene from cyclohexene, of carbon dioxide and allyl alcohol from glyceryl oxalate, and of methane, ethylene, and formaldehyde or hydrogen, ethylene, and acetaldehyde from ethyl ether. In this last case, the chief reaction is 1-2 splitting to ethane and acetaldehyde.

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³ Sherman and Eyring, *J. Am. Chem. Soc.* **54**, 2561 (1932).

⁴ Cf. Gault and Hessel, *Ann. chim. [10]* **2**, 376 (1924), who postulated a similar process to account for the production of hydrogen in the pyrolysis of hexadecane.

⁵ Frey and Hepp, *Ind. Eng. Chem.* **25**, 441 (1933).

⁶ F. O. Rice, *J. Am. Chem. Soc.* **55**, 3035 (1933).

⁷ Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

On the Concentration of Deuterium by Electrolysis

Bleakney and Gould¹ have raised the question as to the reason for the low concentration of deuterium in commercial electrolytic cells as is shown by the analysis of hydrogen obtainable commercially. They point out that this low concentration would imply that this tank hydrogen has all come from apparently new cells.

The specific gravity of water which was distilled from electrolyte which was kindly furnished by the Pittsburgh plant of the Burdett Hydrogen and Oxygen Company has been obtained. This water was carefully purified by distillation through a still which is used for the production of conductivity water, and then deaerated. The specific gravity was obtained by means of a buoyancy balance

similar to that described by Lewis and Macdonald.² Six cells were sampled and the specific gravity obtained was 1.000013 compared to ordinary conductivity water at 18.2°C. The results on all samples agreed to about one part in a million.

The cells from which the electrolyte was taken had been in operation for about five years without the electrolyte having been renewed. A simple calculation showed that

¹ Walker Bleakney and Austin J. Gould, *Phys. Rev.* **44**, 268 (1933).

² G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.* **1**, 341 (1933).