[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

# The Kolbe Hydrocarbon Synthesis in Liquid Ammonia

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Work previously carried out in this Laboratory[2] has demonstrated that the acid nitriles are acid anammonides, since they react with potassium amide in the sense of the equation

$$R\cdot CN + KNH_2 = R\cdot C(=NH)NHK \qquad (1)$$

to form salts of fatty acids of the ammonia system. The present work was undertaken to see whether the electrolysis of liquid ammonia solutions of these salts would yield hydrocarbons in the manner of the Kolbe electrosynthesis in water, that is, in accordance with the equation

$$2R\cdot C(=NH)NH^- \xrightarrow{\text{at anode}} 2NCNH_2{}^{3} + R\cdot R \qquad (2)$$

## Apparatus and Manipulation

The Pyrex electrolytic cell shown in Fig. 1 is approximately 4 × 40 cm. in over-all dimensions. The anode compartment, G (2.1 cm. diameter), is separated from the cathode compartment by a moderately coarse thick sintered Pyrex diaphragm, K. The anode found most suited to the work was a thick piece of platinum wire, I. The cathode was a sheet of platinum foil, J (about 1 cm. wide), surrounding the anode compartment, G, and connected to the external electrical circuit by means of a platinum wire passing through the small ground joint, C. The anode makes contact with a column of mercury in H and this in turn is connected with the other side of the electrical circuit through a suitable variable resistance, ammeter and copper coulometer. Liberated gases pass through M and N to the collectors, O and O′. Since it is necessary to equalize the pressure in the anode and cathode compartments as well as possible to minimize the mechanical transfer of liquid across the diaphragm, the height of mercury in the traps above Q and Q′ is adjustable and an additional smoothing out of pressure fluctuations is effected by the mercury seals, L. In preparation for a run, the cell is thoroughly cleaned and dried, placed in position in the Dewar vessel, E, and a stream of dry ammonia passed through N′, F, K, G and out at M and N. Then the ground caps A and N′ are removed to allow the introduction of metallic potassium into the cell, the metal being filtered through a capillary directly into each compartment.[4] A and N′ are replaced and liquid ammonia then run into E through a tube (not shown) passing through the rubber stopper, D. Another tube passes through D and is connected to the waste in order to dispose of ammonia gas. When about 15 cc. of ammonia has condensed in G (and therefore about 35–40 cc. in F) small quantities of iron oxide are introduced into each compartment, followed, after the formation of potassium amide, by dried nitrile in somewhat less than the theoretical quantity (see equation 1). Ammonia from each compartment is allowed to boil into O and O′ until all gas is absorbed, whereupon suction is applied at R with the stopcocks at the top of O and O′ open, to fill the collectors with acidulated water (P and P′ are attached to water leveling bulbs, Q and Q′ to leveling bulbs containing mercury). The two stopcocks are then closed, and the electrolysis begun, adjusting the current to the desired strength and keeping it at this point as closely as possible throughout the run by means of the rheostat. The ammonia bath in the Dewar is boiled under diminished pressure to minimize the heating effect during electrolysis, and to prevent the formation of bubbles of vapor on the lower surface of the diaphragm (temp. of ammonia in bath about −40 or −50°).

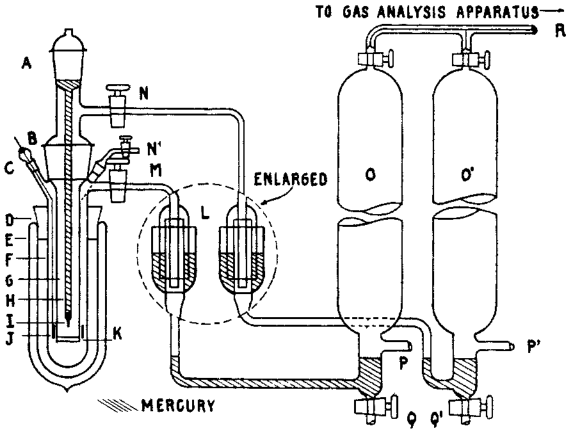

Fig. 1.

Gases in O and O′ are transferred through the capillary R to a modified Shepherd-Porter apparatus (not shown)[4,5] where the individual hydrocarbons are separated by liquid air fractionation. The hydrocarbon fractions obtained from several runs are combined to provide sufficient gas for the vapor density determinations. Attempts were made to determine unsaturated hydrocarbons by allowing the separate fractions to stand for some hours in contact with bromine and water, but none were found.

At the end of an electrolysis, the anode compartment is removed from the cell, and its contents hydrolyzed with a mixture of water and benzene. The aqueous solution is separated, diluted and almost neutralized with dilute nitric acid. Then an excess of ammonia water is added, followed by an aqueous solution of silver nitrate to precipitate yellow disilver cyanamide (silver ammonocarbonate), which is filtered, washed, dried in a vacuum at 60° and weighed.

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(1) From the doctoral dissertation of R. A. Fulton.

(2) Cornell, THIS JOURNAL, **50**, 3311 (1928); Franklin, Eighth International Congress Applied Chem., VI, 123 (1912); *cf.* Ziegler and Ohlinger, *Ann.*, **495**, 99–106 (1932).

(3) Cyanamide is an ammonocarbonic acid, Franklin, THIS JOURNAL, **44**, 486–509 (1922).

(4) Fulton and Bergstrom, THIS JOURNAL, **53**, 3095 (1931).

(5) Shepherd and Porter, *Ind. Eng. Chem.*, **15**, 1143 (1923).

The determination of cyanamide by this method is of course not altogether accurate.[6]

## Experimental Results

All of the experiments listed in Table I are the average of three to five runs, with the exception of Nos. 10 and 11 which are based on single determinations. The conditions of the runs were as nearly the same as possible, except for some variations in the current density.

TABLE I

| No. | Nitrile | R·CN in anode compt., m. moles | K in anode compt., m. atoms | Milli-faradays of electricity | Current density amps./cm.$^2$ | Milli-moles nitrogen | Milli-moles methane | Milli-moles ethane | Mol. wt. of hydrocarbons found | Disilver cyanamide, m. moles |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3CN$ | 51.2 | 60.6 | | 0.20 | All nitrogen | | | | |
| 2 | $CH_3CN$ | 55.9 | 64.2 | 3.360 | .32 | 7.87 | | 1.42 | 29.9 | 2.876 |
| 3 | $CH_3CN$ | 66.9 | 79.0 | 4.066 | .41 | 5.63 | 0.80 | 1.37 | 15.9 28.8 | 3.685 |
| 4 | $CH_3CN$ | 61.2 | 76.0 | 3.549 | .47 | 4.38 | 1.66 | 0.46 | 15.8 29.0 | 3.035 |
| 5 | $CH_3CN$ | 59.3 | 71.4 | 2.434 | .53 | 3.54 | 2.29 | 0.10 | 15.9 28.8 | 2.567 |
| 6 | $C_2H_5CN$ | 40.5 | 40.2 | 6.759 | .21 | 3.04 | 1.71 | 2.80 | 15.9 29.2 | 7.608 |
| 7 | $C_2H_5CN$ | 39.8 | 41.4 | 7.295 | .33 | 1.59 | 3.74 | 1.68 | 16.0 28.9 | 7.219 |
| 8 | $n$-$C_3H_7CN$ | 34.1 | 44.0 | 1.061 | .21 | 4.48 | 0.63 | Trace | 16.0 | 0.840 |
| 9 | $n$-$C_4H_9CN$ | 39 | 51 | 2.835 | .32 | 4.50 | .08 | 1.12 | 15.9 30.0 | 2.496 |
| 10 | $CH_3CN$[a] | 232 | 358 | 12.75 | .32 | 0.85 | .37 | 6.74 | 16.1 29.9 | 14.35 |
| 11 | $C_6H_5CN + KNH_2$, equiv. amt. | Only $N_2$ at anode, salt not sufficiently soluble. | | | | | | | | |

[a] In a small autoclave, at room temperature. This will be described at a later date.

## Discussion

It is evident from the table that in the electrolysis of the potassium salts of the acid amidines, hydrocarbons are formed only at high current densities, and with concentrated solutions. At lower current densities, and with the more dilute solutions, nitrogen is practically the only anode gas, corresponding to the fact that oxygen is obtained when dilute aqueous solutions of the alkali salts of the aquo fatty acids are electrolyzed. The electrolysis of the potassium salts of acid amidines containing more than two carbon atoms strangely enough yields only methane and ethane in recognizable amounts, although occasionally very small quantities of higher hydrocarbons are found. Nitrogen is almost invariably obtained in these experiments in amounts greater than can be accounted for by the known number of coulombs passed through the cell. It is probable that this gas for the most part does not arise from any normal electrode reaction, but is the result of a decomposition of the potassium salt of the amidine at the anode. This perhaps is a thermal effect, because the high current density required to produce hydrocarbons causes vigorous boiling within the anode compartment, particularly, and it was occasionally noticed that arcing occurred between the electrodes. Resinous substances usually appeared on the anode in the electrolysis of potassium alkyl amidines containing more than two carbon atoms, this perhaps intensifying the overheating of the electrode surface. A significant portion of the anode product was a blackish tar of high carbon content (93.7–94.9% in experiments 8 and 9), this possibly indicating the formation of carbon itself at the electrode.

## Summary

The potassium salts of the fatty acids of the ammonia system (acid amidines) all give saturated hydrocarbons when electrolyzed in concentrated liquid ammonia solutions with high current densities. Only in the case of the electrolysis of potassium acetamidine was any of the hydrocarbon obtained that might be expected from the equation representing the Kolbe synthesis, $2CH_3\cdot C(=NH)NHK + 2F = CH_3\cdot CH_3 + NH_2CN$ (at anode) + 2K (at cathode). In all other cases, a mixture of methane and ethane resulted, probably because of thermal conditions at the anode which caused a rather deep-seated decomposition of the amidines.

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[6] Buchanan and Barsky, THIS JOURNAL, **52**, 202 (1930).