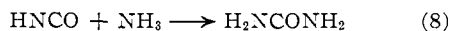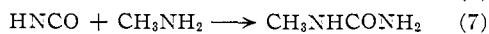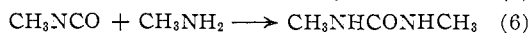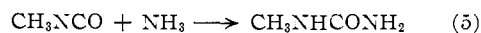shows that methylamine like ammonia is also produced by the base-catalyzed parallel reaction noted above.

The deviation or "sag" between 7.5 and 11 can be interpreted in terms of complicating reactions involving the products. Reactions that can occur in addition to the primary dissociations (eqs. 1 and 2) include

$$CH_3NCO + NH_3 \longrightarrow CH_3NHCONH_2 \quad (5)$$

$$CH_3NCO + CH_3NH_2 \longrightarrow CH_3NHCONHCH_3 \quad (6)$$

$$HNCO + CH_3NH_2 \longrightarrow CH_3NHCONH_2 \quad (7)$$

$$HNCO + NH_3 \longrightarrow H_2NCONH_2 \quad (8)$$

These complications can be minimized by reducing the amount of reactant decomposed. By this technique the concentration of products can be lowered sufficiently to make the rates of these complicating reactions negligible compared to the rates of the primary dissociations (eqs. 1 and 2). Product–time plots at pH 11.1 are shown in Fig. 2. The linearity of these plots shows that, at this pH, conflicting back reactions have been eliminated. An examination of this figure also reveals that the methylamine line can be generated by summing the ordinates of the ammonia line and the cyanate line. This observation coupled with the data in Table I makes it possible to conclude that

$$k_{12} = k_1 + k_2 \quad (9)$$

where k_{12} is a composite constant experimentally equal to k_m. Thus by these data the existence of both primary dissociation reactions (eqs. 1 and 2) is firmly established. As noted earlier (Introduction) Fawsitt measured an over-all rate constant (for eq. 3). On the basis of the arguments presented above this rate constant is equivalent to k_{12}. At 99.2° Fawsitt reports a value of 48.5×10^{-6} min.$^{-1}$ for his first order rate constant calculated on the basis of logarithms to the base ten. Recalculation gives a value of 1.9×10^{-5} sec.$^{-1}$ for k_{12} based on his data. Using our Arrhenius parameters for k_1 and k_2 the value anticipated for k_{12} at 100° was calculated to be 1.6×10^{-5} sec.$^{-1}$. Thus, within combined experimental uncertainties, the results are in essential agreement.

Both primary dissociation reactions proceed more slowly than the decomposition of urea, but of even greater interest is the conclusion that cyanate production (eq. 2) in the absence of base catalysis proceeds from 4–6 times faster (Table I) than ammonia production (eq. 1). For analogous reactions with methylthiourea just the opposite is true. A more detailed discussion of these and other findings will be presented in the last paper of this series.

Electrolytic Oxidation in Liquid Ammonia. I. Carbonic Acid Amides[1]

BY A. F. CLIFFORD AND M. GIMÉNEZ-HUGUET

Amides such as ammonium carbamate and urea have been oxidized electrolytically in liquid ammonia. The product, which appears to be azodicarbonamide, or a condensation (deammonation) polymer of it is isolated as potassium azodicarbonate. Since the electrolysis of hydrazodicarbonamide gives the same product, it is postulated that the oxidation proceeds through a hydrazine derivative. Absorption spectra are reported for the region 200–400 mμ.

Introduction

When concentrated aqueous solutions of sulfates,[2] phosphates,[3] carbonates[4] or borates[5] are electrolyzed with shiny platinum anodes at high current densities, especially in the presence of a non-polarizable anion such as fluoride ion,[6] peroxydisulfates, etc., result.

The process is assumed to consist of the anodic abstraction of an electron from the sulfate ion (for example) to form the sulfate free radical ion, SO_4^-, two of which combine to give the peroxy anion.[7]

The peroxide mechanism of anodic oxidation due to Glasstone and Hickling[8] has been ably refuted by Haïssinsky[9] and by Frumkin, et al.[10]

Similar processes are known involving other elements besides oxygen, e.g., thiosulfate yielding tetrathionate[11] and sulfite yielding dithionate.[12] Thus it seemed reasonable to believe that similar catenation compounds of nitrogen could be formed under suitable conditions by anodic oxidation of amides of the elements S, P, C, B and possibly others. The fact that small amounts of azoben-

(1) This work was supported by the Office of Ordnance Research under Contract No. DA-33-008-ORD-1233 with Purdue University.

(2) K. Elbs and O. Schönherr, Z. Elektrochem., **2**, 245 (1895).

(3) F. Fichter and J. Müller, Helv. Chim. Acta, **1**, 297 (1918).

(4) A. von Hansen, Z. Elektrochem., **3**, 445 (1897).

(5) K. Arndt, ibid., **22**, 63 (1916).

(6) E. Müller, ibid., **10**, 776 (1904); German Patent 155,805 (1904).

(7) F. Richarz, Ann. Physik, **24**, 183 (1885); K. Elbs and O. Schönherr, Z. Elektrochem., **1**, 417, 468 (1894); **2**, 245 (1895); H. Marshall, Proc. Roy. Soc. Edinburgh, **18**, 63 (1891); J. Chem. Soc., **59**, 771 (1891); J. Soc. Chem. Ind. (London), **16**, 396 (1897).

(8) S. Glasstone and A. Hickling, J. Chem. Soc., 2345, 2800 (1932); "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., Inc., New York, N. Y., 1936; Chem. Rev., **25**, 407 (1939).

(9) M. Haïssinsky, Discussions Faraday Soc., No. 1, 254 (1947).

(10) A. N. Frumkin, R. I. Kaganovich, M. A. Gerovich, V. N. Vasil'ev, Doklady Akad. Nauk S.S.S.R., **102**, 981 (1955); C. A., **50**, 3122 (1956).

(11) C. J. Thatcher, Z. physik. Chem., **47**, 641 (1904).

(12) F. Foerster and A. Friessner, Ber., **35**, 2515 (1902); A. Friessner, Z. Elektrochem., **10**, 265 (1904); J. A. V. Butler and W. M. Leslie, Trans. Faraday Soc., **32**, 435 (1936).

zene have been observed[13] to be formed at an iron anode by the oxidation of aniline in alkaline solution lends plausibility to this idea. Similarly the electrolysis of aminedisulfonates, $N(SO_3)_2^{-3}$, in aqueous solution[14] recently has been shown to give hydrazotetrasulfonates.

Electrolyses in liquid ammonia also have been shown to produce nitrogen catenation compounds,[15] although with very poor current efficiencies. Thus hydrazobenzene yielded azobenzene in about 80% conversion and methylaniline yielded N,N'-dimethyl-N,N'-diphenylhydrazine in about 4% conversion. Many other attempts, however, have been fruitless. For example, the anodic oxidation of sulfamide[16] in liquid ammonia produced only nitrogen.

We have found, however, that at voltages sufficiently low the discharge of solvent does not completely outweigh the production of other products, and significant yields of nitrogen catenation compounds can be obtained by electrolysis. The results of the electrolyses of ammonium carbamate and urea will be treated here and the electrolysis of sulfamate in a later paper.

Experimental

Apparatus.—The electrolyses were carried out in a cylindrical cell of 62 mm. diameter made from an inside 71/60 standard taper joint, in which was set a Coors porous porcelain cup. (Porous porcelain was found to be far more satisfactory for diaphragms in liquid ammonia than fritted glass, which disintegrated quite rapidly.) Cylindrical platinum electrodes (6 cm. high) were fitted fairly snugly inside and outside the cup, the internal electrode being the anode. The cell cap was fashioned from an outside 71/60 standard taper joint and carried suspended internally two outside 12/30 standard taper joints for electrode attachments and externally at the center an outside 24/40 standard taper fitting for the single Friedrich condenser equipped with a drainage tube designed to return ammonia over the edge of the porous cup or into the outer (cathode) compartment. All ground glass connections were greased with Fluorolube (Halocarbon Products Corp.) which had been determined to be quite insoluble in liquid ammonia and which completely prevented any freezing of the joints. The reflux condenser was cooled by circulating acetone from a cold bath (Tenney Engineering Corp.) set for −80°. The actual coolant temperature ranged up to −60° depending on the weather and other conditions. This proved to be a very practical set-up and allowed easy removal of the anode liquors merely by lifting out the porous cup.

Preparation of Reagents. Ammonium Carbamate.—This was prepared merely by leading CO_2 into an excess of liquid ammonia. It was not analyzed. It was freely soluble in liquid ammonia. It was soluble to the extent of 3.6 g. per liter in absolute alcohol.

Urea was used as obtained from Fisher Scientific Company.

Hydrazodicarbonamide, Azodicarbonamide and Dipotassium Azodicarbonate.—These substances were prepared according to the method of Thiele.[17] Analyses of these compounds were: for $(HNCONH_2)_2$, C, 20.60%; N, 45.9 ± 2%; H, 5.22%; theoretical: C, 20.3%; N, 47.5%; H, 5.10%; for $(NCONH_2)_2$, C, 21.38%; N, 46.81%; H, 2.97%; theoretical: C, 20.6%; N, 48.2%; H, 3.50; and for $(NCO_2K)_2$, K, 39.35%; N, 11.81%; theoretical: K,

(13) E. Rotondi, *Atti della R. Accademia delle Scienze di Torino*, **39**, 45, Sep.-Abdr.; *Jahresb. Chem.*, 270 (1884); Christeller, Dissertation, Basle, 1900; Klein, Dissertation, Munich, 1902; see A. Moser, "Der elektrolytischen Prozesse der organische Chemie," Halle a/s, 1910, p. 68.

(14) R. R. Grinstead, *J. Inorg. & Nuclear Chem.*, **4**, 287 (1957).

(15) S. Goldschmidt and F. Nagel, *Ber.*, **64B**, 1744 (1931).

(16) J. H. Shroyer, M.S. Thesis, University of Chicago, August, 1928.

(17) J. Thiele, *Ann.*, **271**, 127 (1892).

40.21%, N, 14.43%. The two amides were freely soluble in liquid ammonia and dimethylformamide, and sparingly soluble in water (2 g. per liter and 0.9 g. per liter, respectively) and in ethanol (0.6 g. per liter and 0.02 g. per liter, respectively), but essentially insoluble in CCl_4, dibutyl phthalate, triethyl phosphate and diethylene glycol dimethyl ether. Potassium azodicarbonate did not dissolve appreciably in liquid ammonia, was moderately soluble in ethanol (2.3 g. per liter) and was decomposed by water. It was, however, as reported by Thiele, fairly stable in 30% aqueous potassium hydroxide and quite soluble (greater than 25 g. per liter).

Absorption Spectra of Starting Materials.—The absorption spectra of these substances were determined between 200 mμ and 400 mμ since they were of value in identifying and assaying possible products. The spectra of azodicarbonamide and potassium azodicarbonate agreed substantially with those of Hantzsch and Lifschitz.[18] In the case of the azodicarbonate the range was extended below that of Hantzsch and Lifschitz (about 235 mμ) and a new, intense peak was found at 223 mμ with a minimum at 213 mμ. The extinction coefficient of the peak at 223 mμ could not be determined because of the interference of CO_3^{-2} inevitably present. The absorption band about 400 mμ was used for assay purposes. It was shown to obey Beer's law for concentrations less than 15 mg. per ml. At 400 mμ ε = 0.1278 mg.$^{-1}$ cm.$^{-1}$, as determined on a Cary recording spectrophotometer, Model 10-11M, and 0.1265 mg.$^{-1}$ cm.$^{-1}$, as determined with a Bausch and Lomb Spectronic 20, the instrument which was used for assay. The curve for hydrazodicarbonamide showed three low shoulders about 265, 258 and 250 mμ and general absorption below 210 mμ.

The Electrolyses.—Early in the course of this work a current-voltage curve was taken, using a vacuum-tube volt meter, on the electrolysis of $NH_4SO_3NH_2$ in liquid ammonia to determine (a) whether any process other than discharge of the solvent ($4 NH_3 − 3e^- \rightarrow {}^1/_2 N_2 + 3NH_4^+$) was taking place and (b) if so, what would be the optimum voltage for obtaining other products. The occurrence of a shoulder in the curve about 1.2 volts showed definitely that some process other than discharge of the solvent was occurring. Although, judging from the curve, the optimum ratio of product to nitrogen would have been obtained between 1.0 and 1.5 volts, in practice voltages between 1.5 and 3.0 volts were used for both the carbon amide and sulfur amide runs because of the shorter time required to produce detectable amounts of product. Most of the later runs were carried out at 3.0 volts with anode current densities averaging 0.04 amp. per cm.^{2}

With the exception of two runs on $NH_4SO_3NH_2$ in Divers' liquid at 0° all electrolyses were carried out at the boiling point of the solutions (about −33°) under reflux. An inert or carrier electrolyte was added to both compartments —NaF (saturated, 0.35 g. per 100 g. NH$_3$ at 25°)[19] or NH$_4$F (saturated) in the early experiments, but in the later, NH$_4$Cl (1-2 g. per 100 ml. NH$_3$). The material to be electrolyzed was added to the anode compartment. The cell was closed and ammonia was condensed into the cell by means of the reflux condenser. Electrolyses were continued up to 96 hr. in some cases but averaged 24-36 hr. Attack on the electrodes was very slight even over a long period of time. The yellow products were found either deposited on the anode (at low ammonium salt concentration) or in solution.

Several methods of recovering the products were used. (1) The insoluble deposit on the anode was treated directly with 30% KOH. Organic solvents and distilled water were found not to have any effect on it. (2) Evaporation of the anolyte to obtain the ammonia-soluble product with subsequent dissolution of the residue in water, alcohol, dimethylformamide or 30% aqueous KOH was used in some runs but was not always satisfactory because of loss of product during evaporation, presumably by solvolysis. (3) The anolyte liquor frequently was poured directly into ethanol or into 30% aqueous KOH, thus by-passing the evaporation step.

Absorption Spectra of Electrolysis Products.—Spectra were obtained on the electrolysis products both as dissolved directly in organic solvents, in which case they may be presumed to have been the unchanged products of the elec-

(18) A. Hantzsch and J. Lifschitz, *Ber.*, **45**, 3011 (1912).

(19) "Systematic Inorganic Chemistry," D. M. Yost and H. Russell, Jr., Prentice-Hall, Inc., New York, N. Y., 1946, p. 149.

trolysis, or as dissolved in 30% aqueous KOH, which would have changed any amides to carbonates, or as dissolved in water, in which azodicarbonates would have been destroyed, but in which azodicarbonamide would have been preserved. The spectra were found to agree with those of the synthesized compounds reported above.

Isolation and Analysis of Electrolysis Products.—The products were purified as described below and then analyzed by the departmental microanalyst. Potassium azodicarbonate was precipitated by dissolving the anolyte in cold, concentrated (50%) aqueous KOH and was purified by leaching with ethanol, which removed KOH, $NH_4CO_2NH_2$, $CO(NH_2)_2$ and NH_4Cl. The product analyzed K, 39.28%, N, 13.21%; theoretical: K, 40.21%; N, 14.43%.

Azodicarbonamide, the supposed primary product, was never isolated.

Current Yields.—Current yields were determined for some of the electrolyses by dissolving the total product in 30% aqueous KOH and determining the absorbance at 400 mμ. Current yields for azodicarbonamide (or azodicarbonate) production from ammonium carbamate solutions (3 g./ 100 ml. of NH_3) or urea solutions (3 g./100 ml. of NH_3) containing 2 g. of NH_4Cl per 100 ml. and electrolyzed at 3.0 volts for 24 hr. were on the order of 8%, the rest of the current producing N_2. Since no studies have as yet been made on the effect on current yield of such variables as voltage, NH_4Cl concentration, etc., it cannot be said whether this is the best yield obtainable. In all probability the yields can be improved substantially.

Results

Electrolysis of ammonium carbamate, NH_4-CO_2NH_2, produced a yellow substance which was completely soluble in liquid ammonia if a high concentration of NH_4Cl (2 g. per 100 ml.) were present, but which largely deposited in insoluble form on the anode when only half as much NH_4Cl or NH_4F was present. The anode deposit proved to be insoluble in and undecomposed by water and all organic solvents tried, but reacted with and dissolved in 30% aqueous KOH to give a solution having the absorption spectrum of the azodicarbonates (weak broad maximum near 400 mμ and intense, sharp maximum at 223 mμ).

The anolyte solution, when evaporated and the residue dissolved in water or ethanol, gave the spectrum of azodicarbonamide characteristic of that solvent. If, on the other hand the product were treated with 30% aqueous KOH, a solution having the spectrum of the azodicarbonates was obtained. Since azodicarbonamide is hydrolyzed by 30% aqueous KOH to potassium azodicarbonate, it may be assumed that the primary product was azodicarbonamide. As indicated in the Experimental section, the identity of the azodicarbonate was verified by isolation and analysis.

Another possible product, azodicarbonamidine, $H_2NC(NH)N=NC(NH)NH_2$, could not have been produced, since it was found not to be hydrolyzed with KOH under the conditions used to obtain azodicarbonate from the anolyte.
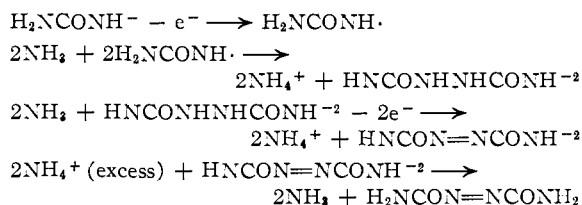
All the observations made on the electrolysis of ammonium carbamate were repeated when urea was electrolyzed. That the carbamates should easily ammonolyze to carbonamides at some stage during the electrolysis is not surprising if it be realized that even in aqueous solution when an alternating current is passed through a solution of ammonium carbamate urea is formed.[20] Urea is also produced at the anode when direct current is

passed through an *aqueous* solution of ammonium carbonate containing excess ammonia.[21]
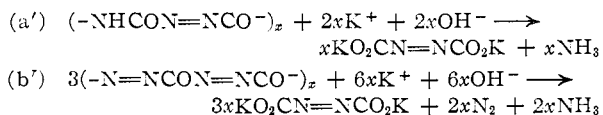
In order to gain some knowledge of the possible course of reaction, hydrazodicarbonamide also was electrolyzed under the same conditions. The products were found to be the same as with urea and ammonium carbamate.

Discussion

The proposed course of the electrolysis of urea is, therefore

$$H_2NCONH^- - e^- \longrightarrow H_2NCONH \cdot$$

$$2NH_3 + 2H_2NCONH \cdot \longrightarrow$$
$$2NH_4^+ + HNCONHNHCONH^{-2}$$

$$2NH_3 + HNCONHNHCONH^{-2} - 2e^- \longrightarrow$$
$$2NH_4^+ + HNCON=NCONH^{-2}$$

$$2NH_4^+ (excess) + HNCON=NCONH^{-2} \longrightarrow$$
$$2NH_3 + H_2NCON=NCONH_2$$

But in the absence of a high NH_4^+ concentration either (a) $x H_2NCON=NCONH_2 \rightarrow (-NHCON= NCO-)_x + xNH_3$ because of the low ionic strength or (b) $4xNH_3 + xH_2NCON=NCONH_2 - 4 xe^- \rightarrow (-N=NCON=NCO-)_x + 4xNH_4^+$. Increased NH_4^+ concentration should inhibit the formation of either of the polymers, as was observed. Either polymer should react with aqueous KOH to give potassium azodicarbonate, as observed.

$$(a') \quad (-NHCON=NCO-)_x + 2xK^+ + 2xOH^- \longrightarrow$$
$$xKO_2CN=NCO_2K + xNH_3$$

$$(b') \quad 3(-N=NCON=NCO-)_x + 6xK^+ + 6xOH^- \longrightarrow$$
$$3xKO_2CN=NCO_2K + 2xN_2 + 2xNH_3$$

Polymer b, however, which could decompose without rearrangement to CO + N_2, seems much less probable than polymer a. Inasmuch as amides frequently condense to polymers at slightly elevated temperature (e.g., 2 $CO(NH_2)_2 \rightarrow HN-(CO_2NH_2)_2 + NH_3$) the same type of process may reasonably be expected at an electrode (cf. the $(NH_4)_2CO_3$ and $NH_4CO_2NH_2$ to urea cases cited[20,21]).

The electrolysis of ammonium carbamate must proceed in exactly the same manner except for an additional ammonolysis step somewhere along the way.

Catalysis of the Anodic Decomposition of the Solvent.—All of the successful runs described above were made with ammonia from the same cylinder. When ammonia cylinders were changed, however, all production of azo compounds ceased and attack upon the platinum anode became heavy. Neither addition of water to the solutions nor exhaustive drying of the ammonia over sodium had any appreciable effect. Completely new apparatus likewise made no difference. Similar results in other laboratories make it seem highly probable that traces of some as yet unidentified material catalyze the preferential release of nitrogen resulting in drastically reduced production of catenation compounds. That this is a reasonable explanation is indicated strongly by the following information from the literature. In the electroly-

(20) E. Drechsel, *J. prakt. Chem.*, **22**, 476 (1880).

(21) F. Fichter, *Z. Elektrochem.*, **24**, 41 (1918); F. Fichter, H. Steiger and T. Stanisch, *Verhandl. Schweiz. Naturforsch. Ges.*, **28**, ii, 66 (1916).

sis of ammonia solutions of $NaGe(C_6H_5)_3$, it was found[22] that the amount of nitrogen liberated was almost equivalent to the amount of $(C_6H_5)_3GeH$ produced (the other anode product being $(C_6H_5)_3$-$GeGe(C_6H_5)_3$) if a platinum anode was used, whereas on a mercury anode the amount of nitrogen produced was much less. Perhaps more significant are the experiments of Browne and Holmes[23] who found that upon electrolysis of an ammonia solution of ammonium azide, the ratio of hydrogen to nitrogen produced was high (as high as 1.8) when a platinum anode was used, indicating considerable oxidation of the solvent, whereas with a graphite anode the ratio was about 0.33, indicating

(22) L. S. Foster and G. S. Hooper, THIS JOURNAL, **57**, 76 (1935).
(23) A. W. Browne and M. E. Holmes, *ibid.*, **35**, 672 (1913).

virtually quantitative oxidation of the azide ion and no solvent discharge.

Summary.—It can now be seen that the expected analogy between the anodic discharge of oxy anions in water solution to give peroxy anions and the anodic discharge of amides in ammonia to give hydrazine derivatives is established. In the case of the hydrazo compounds, however, further oxidation takes place so readily as to preclude isolation of the hydrazine derivatives, the corresponding azo compounds being found instead.

With improvement of yields, this should be an attractive route to many azo compounds, both known and unknown.

LAFAYETTE, INDIANA

Mechanism Studies of the Fischer–Tropsch Synthesis: The Incorporation of Radioactive Ethylene, Propionaldehyde and Propanol

BY W. KEITH HALL, R. J. KOKES[1] AND P. H. EMMETT[1]

When a $1:1 = H_2:CO$ synthesis gas containing 1 to 1.25 mole % radioactive ethylene is passed over an iron catalyst at 224°, about 12% of the hydrocarbons formed at 1 atm. stem from the ethylene. At 100 p.s.i., about 6% of the hydrocarbons are formed from ethylene. When 1.5% radioactive propanol or propionaldehyde is added to the synthesis stream, at one atmosphere almost half of the hydrocarbons come from the additive. In the case of 1-propanol the butanes and butenes formed from the additive are predominantly straight chain. These results, taken as a whole, show that ethylene can act as a chain initiator although not to the same extent as primary alcohols. The available data for such tracer experiments are re-examined in view of this new result, and a mechanism is suggested for iron catalysts which is consistent with the tracer experiments and with the available kinetic data for the Fischer–Tropsch synthesis and for the carbiding of iron catalysts. This mechanism successfully predicts the isomer and carbon number distributions found for Fischer–Tropsch products.

Introduction

In spite of the apparent complexity of the Fischer–Tropsch reaction, it is possible to explain many experimental facts on the basis of the relatively simple mechanism postulated by Storch, Golumbic and Anderson,[2a] as modified by Kummer and Emmett.[3] According to this picture, the carbon monoxide and hydrogen react on the surface to form a species similar to adsorbed methanol.[2a] These C_1 surface complexes then react by splitting out water to form a C_2 complex similar to adsorbed ethanol.[3] The production of higher molecular weight products is presumed to occur by the reaction of C_n with C_1 complexes to form water and C_{n+1} complexes. The synthesis products may be formed by direct desorption of these complexes or by dehydration, dehydrogenation, hydrogenation, etc., followed by desorption. It has been shown[4] that this mechanism leads to a two parameter equation which quite adequately describes the isomer and carbon number distributions of the hydrocarbon products obtained from synthesis over iron and cobalt catalysts.

(1) John Hopkins University, Baltimore, Maryland.
(2) H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer–Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951; (a) p. 591 ff.; (b) p. 538 ff.
(3) J. T. Kummer and P. H. Emmett, THIS JOURNAL, **75**, 5177 (1953).
(4) R. B. Anderson, R. A. Friedel and H. H Storch, *J. Chem. Phys.*, **19**, 313 (1951).

Recent tracer experiments[3,5-7] have furnished support for this picture and, in addition, have made apparent several additional features of the mechanism. These experiments have definitely shown that primary alcohols tend to act as chain initiators for the synthesis of higher molecular weight hydrocarbons. With adsorbed methanol, the C_1 complex formed acts (more often) as a chain initiator, but also as a chain build-in unit; a similar result was obtained with gaseous formaldehyde, suggesting that the C_1 chain initiator may not be identical with the C_1 build-in unit and that several distinct C_1 complexes exist. Also in the case of the C_2 complex, some species (possibly ethylene) other than adsorbed ethanol acts as a chain initiator.[7]

In an effort to clarify further the reaction mechanism over iron catalysts, a series of tracer experiments has been carried out with radioactive ethylene to determine whether or not it can function as a C_2 chain initiator. In addition, an earlier tracer experiment was repeated to check a result of Kummer and Emmett,[3] that indicated (in conflict with the simple theory[2,3]) that when labeled 1-propanol was added to the synthesis stream, some

(5) J. T. Kummer, H. H. Podgurski, W. B. Spencer and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).
(6) W. K. Hall, R. J. Kokes and P. H. Emmett, *ibid.*, **79**, 2983 (1957).
(7) R. J. Kokes, W. K. Hall and P. H. Emmett, *ibid.*, **79**, 2989 (1957).