[CONTRIBUTION OF SYNTHETIC FUELS RESEARCH BRANCH, BRUCETON, PENNA.]

Studies of the Fischer–Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis[1]

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Changes in the composition of nitrided iron catalysts during use in the Fischer–Tropsch synthesis at 7.8 and 21.4 atmospheres operating pressure are described. The ε-nitrides are slowly converted to ε-carbonitrides, the rate of replacement of nitrogen by carbon being somewhat more rapid at 21.4 than at 7.8 atmospheres. At the lower operating pressure, oxidation and deposition of elemental carbon proceed at a very slow rate, whereas at 21.4 atmospheres these reactions are considerably more rapid in some catalysts. At the higher pressure, the type of structural promoter appears to be important in determining the rates of oxidation and of deposition of free carbon. When used nitrided catalysts are treated with hydrogen, the nitrogen is almost completely removed whereas the carbon content is not greatly changed. A part of the carbon appears either as Hägg carbide or as cementite depending upon the temperature of hydrogenation.

In a previous paper,[2] a description was given of the composition and phase changes of a reduced fused catalyst which was used in the synthesis at 7.8 atmospheres. The magnetite content of that catalyst increased throughout the experiment until it constituted more than 35% of the iron after 50 days of synthesis. In the synthesis at 21 atmospheres, the oxidation of a reduced catalyst was considerably more rapid. The present paper deals with changes in the composition of nitrided iron catalysts during the synthesis; and it will be seen that these catalysts oxidize at a much slower rate than reduced catalysts under corresponding conditions. Nitrided catalysts are more active, in many cases, than corresponding reduced catalysts[1,3] and yield a product of lower molecular weight containing a high percentage of oxygenated compounds.

Experimental

The composition and preparation, methods of pretreating, and testing and sampling of catalysts have been described in earlier papers[1-7] with the exception of the composition of fused catalyst L3028 which contained 100Fe:3.9ZrO_2:0.51K_2O. This preparation was reduced in hydrogen at 450°, whereas the other fused catalysts, D3001 (Fe_3O_4–MgO–K_2O) and D3008 (Fe_3O_4–Al_2O_3–K_2O), were reduced at 550°. Sintered catalyst A2106.11 (Fe_3O_4–K_2CO_3) and precipitated catalyst P3003.24 (Fe_3O_8–CuO–K_2CO_3) were reduced at 400 and 300°, respectively. The reduced catalysts were converted to ε-nitrides by treatment with high flows of ammonia at temperatures varying in individual experiments from 300–385°. The activity and selectivity of the nitrided catalysts were relatively independent of nitriding temperature. All catalysts were 6–8 mesh, except P3003.24 which was 6–10 mesh. The space velocity during the synthesis was usually maintained constant, and the temperature was varied to maintain carbon dioxide-free contractions of about 65%.

For chemical analysis, samples of used catalysts were extracted with boiling toluene to remove adsorbed synthesis products; the extracted material was then analyzed for total iron, carbon and nitrogen. Particular care was taken to remove the solvent and to prevent atmospheric oxidation of the catalyst. Oxygen values, determined by difference, are the most uncertain data because they contain the combined errors of all of the other determinations. From the weight percentages of iron, carbon, nitrogen and oxygen, the atom ratios of carbon to iron, nitrogen to iron, and oxygen to iron were computed.

The phases present in pretreated and in used catalysts were identified by X-ray diffraction photograms[8] which showed that the used nitrided catalysts usually contained ε-carbonitride and magnetite, but no α-iron. For quantitative estimation, the phases containing iron were assumed to be magnetite and ε-carbonitride,[8a] the latter being arbitrarily assumed to be a mixture of Fe_2C and Fe_2N.[9] From the atom ratios of total carbon, of nitrogen, and of oxygen to iron, the percentages of iron as Fe_2C, Fe_2N and Fe_3O_4 were computed. When the sum of the percentages of iron in these phases exceeded 100, the apparent excess was attributed to the presence of elemental carbon, and an atom ratio of elemental carbon to iron was computed. The above calculation was made only for samples containing essentially ε-carbonitride and magnetite.

Results

Test X218 with fused catalyst D3001 using $1H_2$ to 1CO gas at 7.8 atmospheres (Fig. 1) was the most detailed study of the changes of catalyst composition during synthesis; and it represents the usual behavior of nitrided catalysts at this pressure. The pretreated catalyst contained atom ratios of N/Fe = 0.43 and O/Fe = 0.05. Only the pattern of ε-nitride was observed by X-ray diffraction analysis. For the first 98 days of synthesis, the temperature was maintained at about 217°, and the activity was essentially constant. The nitrogen to iron ratio decreased while the total carbon to iron ratio increased, the rates of these processes being rapid at the beginning of the test and decreasing with time. The atom ratios of elemental carbon to iron and of oxygen to iron increased from 0.0 to 0.10, and from 0.05 to about 0.14, respectively, during that time. As shown in Fig. 1, 10% of the iron was present as magnetite and 90% as ε-carbonitride after 98 days of testing. Of the interstitial atoms, 37% was carbon and 63% nitrogen. During the remainder of the test (99

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(1) Previous paper of this series, J F. Shultz, B. Seligman, L. Shaw and R. B. Anderson (submitted to *Ind. Eng. Chem.*).

(2) R. B. Anderson, L. J. E. Hofer, E. M. Cohn and B. Seligman, THIS JOURNAL, **73**, 944 (1951).

(3) R. B. Anderson, J. F. Shultz, B. Seligman, W. K. Hall and H. H. Storch, *ibid.*, **72**, 3502 (1950).

(4) R. B. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

(5) A. Krieg, A. P. Dudash and R. B. Anderson, *ibid.*, **41**, 1508 (1949).

(6) H. H. Storch, *et al.*, Bureau of Mines Technical Paper, 709 (1948).

(7) R. B. Anderson, B. Seligman, J. F. Shultz, R. E. Kelly and M. A. Elliott, (submitted to *Ind. Eng. Chem.*).

(8) X-Ray diffraction patterns of nitrides, carbonitrides and carbides of iron have been described by K. H. Jack, *Proc. Royal Soc.* (*London*), **195A**, 34, 41, 56 (1948). X-Ray studies of carbides of iron have been reported by L. J. E. Hofer, E. M. Cohn and W. C. Peebles, THIS JOURNAL, **71**, 189 (1949).

(8a) The possibility that used catalysts may contain ferrous or promoter carbonates was examined by determining the carbon dioxide liberated when the sample was digested in hydrochloric acid. Less than 1% CO_2 by weight was found except for samples of tests X349 and X226 (Table I) for which the carbon dioxide was 4.36 and 4.92%, respectively. Carbon dioxide values of about 1% produced no significant variations of the calculated composition data. However, in the calculations of X349 and X226 the carbon dioxide was assumed to be present as $MgCO_3$, since sizable CO_2 values were obtained only for catalyst containing magnesia.

(9) These formulas correspond to the upper limit of the ε-carbonitride phase.

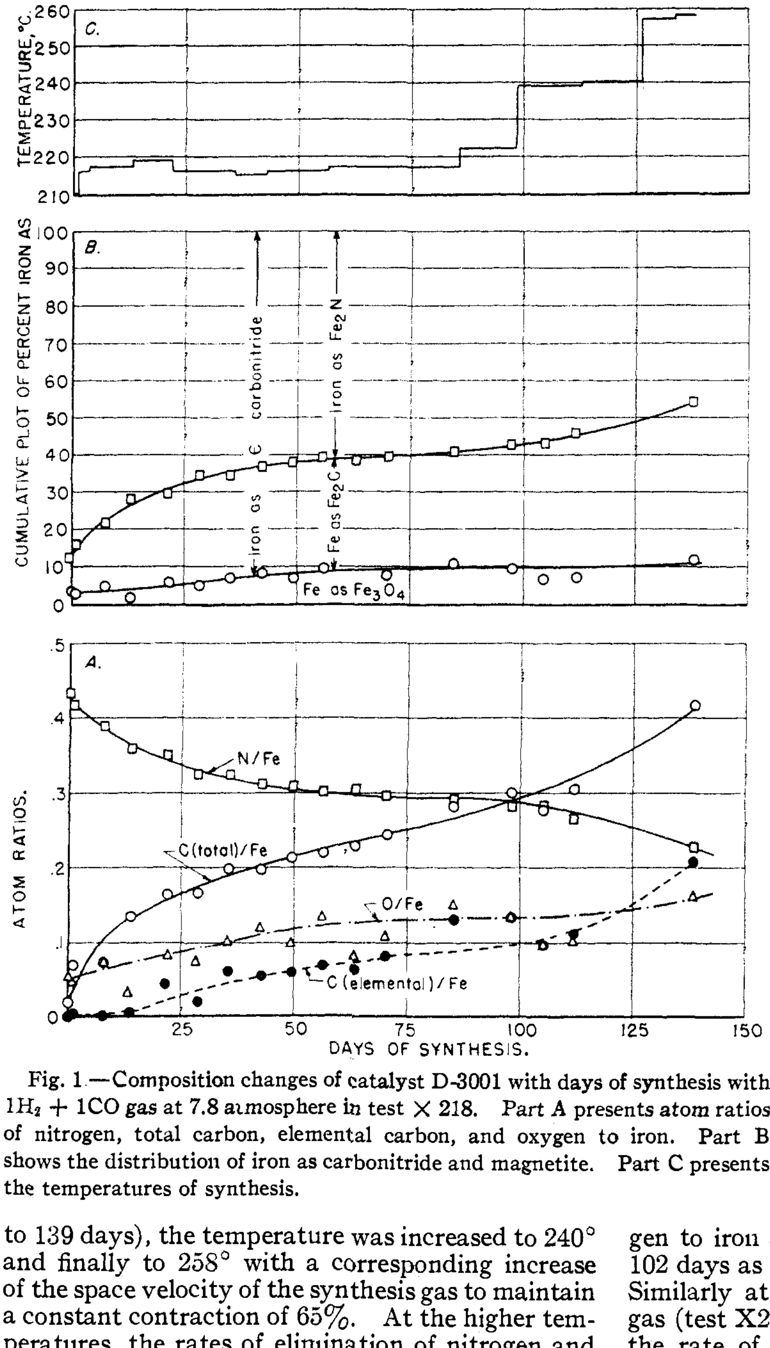

Fig. 1.—Composition changes of catalyst D-3001 with days of synthesis with $1H_2 + 1CO$ gas at 7.8 atmosphere in test X 218. Part A presents atom ratios of nitrogen, total carbon, elemental carbon, and oxygen to iron. Part B shows the distribution of iron as carbonitride and magnetite. Part C presents the temperatures of synthesis.

to 139 days), the temperature was increased to 240° and finally to 258° with a corresponding increase of the space velocity of the synthesis gas to maintain a constant contraction of 65%. At the higher temperatures, the rates of elimination of nitrogen and addition of carbon were greater. The oxygen to iron atom ratio increased only slightly, whereas the elemental carbon to iron ratio increased from about 0.1 after 98 days to 0.2 after 139 days. The X-ray photograms always showed a well-defined pattern of ε-carbonitride which was the only detectable phase in most cases, although an additional weak magnetite pattern was observed in a few samples.

Table I presents analytical data for other tests of catalyst D3001 at 7.8 and 21.4 atmospheres. In test X215 after 203 days of operation, the catalyst still showed only an X-ray diffraction pattern of ε-carbonitride and contained small amounts of elemental carbon and oxide. The catalytic activity remained essentially constant throughout this period. Nevertheless, the catalyst was renitrided after 203 and again after 238 days with ammonia at 350° and at a space velocity of 1000 for 6 hours. After renitriding and use in synthesis, the catalyst still produced an X-ray pattern of only ε-carbonitride. However, the fraction of nitrogen in the carbonitride phase was increased, the oxygen to iron ratio was decreased, and the elemental carbon to iron ratio was increased.

In test X349 at 21.4 atmospheres with $1H_2$ to 1CO gas the nitrogen content of the catalyst decreased more rapidly than at 7.8 atmospheres, and oxidation as well as elemental carbon deposition were faster. After synthesis, the samples gave X-ray patterns of ε-carbonitride, magnetite and α-iron. About 43% of the iron was present as magnetite, and the elemental carbon to iron ratio was 0.059.

In test X226 with $2H_2$ to 1CO gas the amounts of magnetite and elemental carbon found in the used catalyst were less than those observed in X349 with $1H_2$ to 1CO gas. Although in 37 days of test X349 the nitrogen had decreased to about the same value as found after 64 days of X226, it is believed that the removal of nitrogen was relatively independent of synthesis gas composition. As shown in Fig. 1, the nitrogen content decreased rapidly initially and then remained essentially constant (50–99 days) until the temperature of operation was increased. Apparently a constant nitrogen content was also approached at 21.4 atmospheres, since in test X225 which was a duplicate of X349 except for duration, the nitrogen to iron atom ratio was the same (0.139) after 102 days as in X349 (37 days) and X226 (64 days). Similarly at 7.8 atmospheres with $1H_2$ to 1.5CO gas (test X236) the rate of removal of nitrogen and the rate of oxidation were the same as in X218; however, the deposition of elemental carbon was greater with the carbon monoxide rich gas.

Table II presents analytical data for nitrided fused catalysts containing alumina and zirconia as structural promoters as well as data for nitrided sintered and precipitated catalysts. Nitrided catalysts D3008 (Fe_3O_4–Al_2O_3–K_2O) differ from D3001 in being more resistant to oxidation during synthesis at 21.4 atmospheres. Nitrogen was removed from D3008 at a greater rate at 21.4 atmospheres (X337) than at 7.8 atmospheres (X253). Analyses of nitrided, sintered catalyst A2106.11 (Fe_3O_4-K_2O) and nitrided precipitated catalyst P3003.24 (Fe_2O_3–CuO–K_2CO_3) (Table II) again demonstrated that nitrided iron catalysts are resistant to oxidation in the synthesis at 7.8 atmospheres.

TABLE I

COMPOSITION CHANGES IN NITRIDED CATALYST D3001 DURING SYNTHESIS

			Conditions of previous period of testing				Atom ratios to iron				% iron as		
Test	Previous treatment[a]	Total days of synthesis	Temp., °C.	Space velocity[b]	Contraction, %[c]	Phases from X-ray diffraction[d]	Carbon Total	Carbon Elemental	Nitrogen	Oxygen	Fe_2C	Fe_2N	Fe_3O_4
			Operating pressure = 7.8 atmospheres (absolute)										
X215	RN	0	...	...	..	ε	0	0	0.46	0	0	92.0	..
	RNU	203	227	99	65	ε	.324	.090	.194	.192	46.8	38.8	14.4
	RNUN[e] U	238	217	100	64	ε	.355	.175	.266	.146	35.9	53.2	10.9
	RNUN[e] UN[e] U	252	223	101	63	ε	.358	.186	.276	.140	34.3	55.2	10.5
X236[f]	RN	0	...	...	..	ε	0	0	.46	0	0	92.0	..
	RNU	50	230	104	64	ε	.257	.103	.302	.117	30.2	60.4	8.8
			Operating pressure = 21.4 atmospheres (absolute)										
X349	RN	0	...	...	..	ε	0	0	.432	.082	0	86.4	6.2
	RNU	37	241	309	64	ε, M, α	0.239	0.059	.138	.487	36.0	27.6	36.4
X226[g]	RN	0	...	...	..	ε	0	0	.452	.068	0	90.4	5.1
	RNU	64	241	347	54	ε, M, α	0.224	0.000	.140	.329	44.8	28.0	27.2

[a] R = reduced in hydrogen, N = nitrided with ammonia, U = used in synthesis. [b] Space velocity defined as volumes of synthesis gas (S.T.P.) per volume of catalyst space per hour. [c] Apparent carbon dioxide free gas contraction. [d] α = α-iron, ε = ε-nitride or carbonitride, M = magnetite. Phases are listed in order of decreasing amounts. [e] Renitrided at 350° and a space of ammonia of 1000 for 6 hours. [f] Synthesis with $1H_2$ to 1.5 CO gas. [g] Synthesis with $2H_2$ to 1 CO gas.

TABLE II

COMPOSITION CHANGES IN NITRIDED CATALYSTS DURING THE SYNTHESIS

All tests with $1H_2$ to 1CO synthesis gas

				Conditions of previous period of testing					Atom ratios to iron				% iron as		
Test	Catalyst no.	Previous treatment[a]	Total days of synthesis	Pressure, atmospheres	Temp., °C.	Space velocity[b]	Contraction, %[c]	Phases from X-ray diffraction[d]	Carbon Total	Carbon Elemental	Nitrogen	Oxygen	Fe_2C	Fe_3N	Fe_3O_4
X355	L3028	RN	0	..	...	...	..	ε, ?	0	0	0.454	0.082	0	90.8	6.1
		RNU	40	21.4	222	313	66	ε, ?	.186	.055	.286	.219	26.4	57.2	16.4
X253	D3008	RN	0	..	...	...	..	ε	0	0	.434	.090	0	86.8	6.7
		RNU	49	7.8	230	98	63	ε	.178	.060	.334	.131	23.6	66.8	9.6
X337	D3008	RN	0	..	...	...	..	ε	0	0	.438	.099	0	87.6	7.4
		RNU	50	21.4	243	277	65	ε, M, α	.254	.066	.261	.178	37.6	52.2	13.4
		RNUR[e]	50	..	...	...	..	α, C, M	.239	?	.002	.138	?	0.4	10.4
		RNURU	70	21.4	238	297	65	M, α, C	.559	?	.009	.670	?	1.8	50.2
X266	A2106.11	RN	0	..	...	...	..	ε, M	0	0	.470	...	0	94.0	..
		RNU	60	7.8	216	102	65	ε	.160	.074	.369	.120	17.2	73.8	9.0
X273	P3003.24	RN	0	..	...	...	..	ε, Cu, M	0	0	.463	.130	0	92.6	9.7
		RNU	39	7.8	229	138	64	ε, Cu	.230	.109	.318	.163	24.2	63.6	12.2
		RNUR[f]	39	..	...	...	..	α, Cu, X	.241	?	0	.120	?	0	9.0
		RNURU	67	7.8	230	137	65	M, X	.327	?	.002	.749	?	0.4	56.1

[a] R = reduced in hydrogen, N = nitrided with ammonia, U = used in synthesis. [b] Space velocity defined as volumes of synthesis gas (S.T.P.) per volume of catalyst space per hour. [c] Apparent carbon dioxide free gas contraction. [d] α = α-iron, ε = ε-nitride or carbonitride, X = Hägg carbide, C = cementite, M = magnetite and Cu = copper. Phases are listed in order of decreasing amounts. [e] Used catalyst reduced at 385° and a space velocity of hydrogen of 1000 for 4 hours. [f] Used catalyst reduced at 300° and a space velocity of hydrogen of 1000 for 9 hours.

The nitrided catalysts in tests X273 and X337 were reduced with hydrogen after 39 and 50 days of testing, respectively. This treatment removed virtually all of the nitrogen, whereas the carbon was essentially unchanged and the oxygen decreased only slightly. The used, fused catalysts in X337 and in X214[3] contained α-iron, cementite and magnetite (in order of decreasing amounts after reduction at 385°). The used, precipitated catalyst in X273 contained α-iron, copper and Hägg carbide after reduction at 300°. After reduction the products of the synthesis changed from the relatively low molecular weight, highly oxygenated products characteristic of nitrided catalysts to a high molecular weight, slightly oxygenated material characteristic of reduced or carbided catalysts. After several weeks of testing, the principal phase in the reduced nitrides was magnetite which amounted to more than 50% of the iron.

Discussion

When ε-iron nitrides were treated with carbon monoxide at 450° and atmospheric pressure, ε- or ζ-iron carbonitrides were formed[10] in which carbon replaced nitrogen with the ε- and ζ-structure remaining unchanged until more than 75% of the nitrogen was replaced by carbon. Upon further treatment with carbon monoxide, the carbonitride changed to Hägg carbide. With massive iron nitride, no appreciable amount of oxide or elemental carbon was formed in the carburization.[10] Appar-

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(10) K. H. Jack, *Proc. Royal Soc.* (*London*), 195A, 41 (1948).

ently, the substitution reaction also occurs during the synthesis, but concomitantly with oxidation of the catalyst and deposition of elemental carbon. At synthesis temperatures (210–250°), the replacement of nitrogen by carbon proceeded somewhat more rapidly at 21.4 atmospheres than at 7.8 atmospheres, but in every case considerably more slowly than observed by Jack at 450°. The nitrogen content of the catalyst was never decreased below atom ratios of N/Fe of 0.14, nor was Hägg carbide observed in the used nitrided catalysts. Although all the nitrided catalysts were quite resistant to oxidation and deposition of elemental carbon at 7.8 atmospheres, these reactions proceeded much faster in some catalysts at 21.4 atmospheres. However, the stability and activity of nitrided catalysts were much greater at both pressures than those of reduced catalyst. The stability of fused catalysts at 21.4 atmospheres varied considerably with the type of structural promoter. Thus, the catalysts promoted with alumina or zirconia were much more resistant to oxidation than the magnesia-promoted catalyst.

The rate of removal of nitrogen from the catalyst was relatively independent of the composition of the synthesis gas, indicating that the hydrogenation of nitrides was strongly inhibited by carbon monoxide and/or synthesis products. In pure hydrogen, iron nitrides can be completely hydrogenated in a few minutes at synthesis temperatures.

When ε-carbonitrides were reduced in hydrogen, most of the nitrogen was removed; however, the carbon content changed very little, and a part of the carbon appeared as carbide. That cementite was formed in X337 and Hägg carbide in X273 may be attributed to the differences in the temperatures of hydrogenation; however, the differences in catalyst type and composition, especially the presence or absence of copper, may be important in determining the nature of the carbide phase. In subsequent synthesis, the hydrogenated, used catalysts behaved like reduced catalysts in regard to their selectivity and tendency to oxidize.

Acknowledgments.—The authors are pleased to acknowledge the assistance of L. J. E. Hofer and W. C. Peebles in preparing and interpreting X-ray diffraction patterns of catalyst samples, as well as the assistance of W. E. Dieter and W. Oppenheimer in carrying out chemical analyses.

BRUCETON, PENNA. RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DAVIS CAMPUS OF THE UNIVERSITY OF CALIFORNIA]

The Solubility of Toluene in Silver Perchlorate Solutions and the Absorption Spectra of the Toluene–Silver Complexes[1]

BY R. M. KEEFER AND L. J. ANDREWS

The solubilities of toluene in aqueous silver perchlorate–sodium perchlorate solutions of ionic strengths 1 and 5, as influenced by changes in silver ion concentration, have been determined. The ultraviolet absorption spectra of certain of these toluene–silver ion solutions also have been investigated. The results of these studies indicate that 1:1 and probably 2:1 silver ion–toluene complexes are present in these solutions.

The solubilities of a number of benzene derivatives in aqueous solutions containing varying amounts of silver nitrate (and sufficient potassium nitrate to adjust the ionic strength of the solvent to unity) have been measured.[2] The resultant data have been interpreted on the supposition that equilibria (1) and (2) were established in the saturated solutions.

$$Ag^+ + Ar = AgAr^+ \qquad K_1 = \frac{(AgAr^+)}{(Ag^+)(Ar)} \qquad (1)$$

$$Ag^+ + AgAr^+ = Ag_2Ar^{++} \qquad K_2 = \frac{(Ag_2Ar^{++})}{(Ag^+)(AgAr^+)} \qquad (2)$$

To evaluate K_1 and K_2 an additional constant K has been defined as

$$K = \frac{(Ar_c)}{(Ag^+)(Ar)} = K_1 + K_1K_2(Ag^+) \qquad (3)$$

where

(Ar_c) = molar concentration of complexed hydrocarbon = $(Ar_t)-(Ar)$

(Ar_t) = molar concentration of all hydrocarbon containing species

(Ar) = molar concentration of uncomplexed hydrocarbon = molar concentration of hydrocarbon in its saturated solution in 1 N potassium nitrate

(Ag^+) = concentration of free silver ion in solution

The only evidence that Ag_2Ar^{++} actually was formed in these reactions was the fact that K values increased in a linear fashion with increasing silver ion concentration of the solvent, as required by eq. 3.

In the interpretation of the experimental data by the above equations the following assumptions were made regarding the properties of the aromatic substances and of the ions in solutions of different silver ion concentrations (but of fixed ionic strength): (1) The activity of the uncomplexed aromatic substance is the same in all solutions. This was arbitrarily chosen to equal the concentration of aromatic substance in 1 M potassium nitrate. (2) The activity coefficients of the two singly charged ions, $AgAr^+$ and Ag^+, are equal. Thus the calculated values of K_1 based on concentrations would closely approximate the thermodynamic equilibrium constant for eq. 1. The thermodynamic equilibrium constant for eq. 2 would be given by $K_2\,(\gamma_{Ag_2Ar^{++}}/\gamma_{Ag^+}\gamma_{AgAr^+})$. **The activity coefficient term was assumed to be constant as long**

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[1] Paper number VIII in the series "Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds."

[2] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **71**, 3644 (1949); **72**, 3113 (1950); **72**, 5034 (1950).