plotted are those obtained in bulbs 22 liters or larger. The rate constants were extrapolated to 27° using the appropriate energy of activation. By excluding measurements made in small bulbs and by using the appropriate value of k_0, one finds in Fig. 3 an even better description of low-pressure results than is given by Mills and Johnston in their Fig. 7. Thus the slight heterogeneity encountered by Mills and Johnston does not alter their conclusion that Ogg's[3] mechanism predicts the observed behavior of nitrogen pentoxide at all concentrations.[11,12]

Acknowledgment.—This investigation was conducted under the sponsorship of the Office of Naval Research, Contract N6onr-25131, Project NR 058 246.

[11] H. C. Ramsperger and R. C. Tolman, *Proc. Natl. Acad. Sci.*, **16**, 6 (1930).

[12] H. C. Ramsperger, M. E. Nordberg and R. C. Tolman, *ibid.*, **15**, 453 (1929).

STANFORD UNIVERSITY, CALIF. RECEIVED MARCH 27, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange Studies with Complex Ions. II. The Kinetics of the Exchange of Radiocyanide Ion with Potassium Hexacyanomanganate(III) in Aqueous Solution[1]

BY ARTHUR W. ADAMSON, JOAN P. WELKER[2] AND W. B. WRIGHT

The results of a kinetic study of the exchange in aqueous solution between potassium hexacyanomanganate(III) and potassium radiocyanide are reported. The exchange rate is found to be first order in complex ion concentration, and to be independent of the cyanide concentration, of *p*H over the range 9.0 to 10.8, and of ionic strength. It is not photocatalyzed but is slightly dependent upon extent of glass surface. The first order rate constant at 0° is 2.64×10^{-2} min.$^{-1}$ and the activation energy is found to be *ca.* 8.5 kcal./mole. It is proposed that the rate-determining step involves the hepta-coordinated ion $Mn(CN)_6H_2O^{-3}$. The general applicability of a mechanism of this type to the exchange results reported for various tetra and hexa-coördinated cyanides is discussed.

Previous work in these laboratories, comprising determinations of the qualitative exchange behavior of a number of complex ions with respect to radiocyanide ion in aqueous solution,[3] led to the observation of an exchange with the hexacyanomanganate(III) complex which was unexpectedly rapid, if judged by the rates for the corresponding complex ions of Cr(III) and Fe(III). The present paper presents the results of a kinetic study designed to yield information concerning the kinetics, and, if possible, the mechanism for this system.

Experimental

Preparation and Purity of the $K_3Mn(CN)_6$.—Analyses of the compound prepared by the addition of solid manganese-(III) orthophosphate to warm potassium cyanide solution[4] indicated that the complex was only approximately 92% pure, due to the presence of MnO_2.[4] Repeated recrystallizations of the compound from warm 10% potassium cyanide solution did not improve the quality. Because of this difficulty, a different method of preparation,[5] involving the formation and subsequent air oxidation of potassium hexacyanomanganate(II) was employed for the present work. The product was recrystallized once from 10% potassium cyanide solution, washed with alcohol, and then ether, and stored in a vacuum desiccator.

The compound was analyzed by fuming with sulfuric acid, and determining the manganese by the sodium bismuthate method. The result for manganese was 16.67% (calculated for $K_3Mn(CN)_6$, 16.73%).

Counting and Tracer Techniques.—Potassium radiocyanide was prepared from $BaC^{14}O_3$ by the sodium azide method.[6,7] The same counting procedure was employed as that described in the previous paper,[3] except that a windowless, flow type counter (using a 98.7% He, 1.3% butane mixture) was employed instead of a mica end-window tube. The coincidence correction was determined by the same method as before, and since the samples were uniformly about 2 mg./cm.^{2} in thickness it was considered adequate to correct for self-absorption by means of the same curve as previously given.

Exchange Experiments.—The following general procedure was employed for the exchange runs. Solid complex was dissolved in inactive potassium cyanide solution of concentration about 90% of the desired final value, and the mixture brought to and kept at the desired temperature for one-half hour before the addition of sufficient potassium radiocyanide solution to give the indicated final concentrations of free cyanide and of complex. After the lapse of the desired exchange time, the complex was precipitated as the cadmium salt, and the specific activity of the remaining free cyanide determined in the manner previously described.[3] These exchange times were measured from the moment of addition of the tracer until the end of the *ca.* two-minute period of centrifugation of the precipitated complex.

Color Changes.—The solution obtained upon dissolving the complex in dilute potassium cyanide solution initially is an orange-red color, and fades to a pale yellow over a period of 10 to 15 minutes, at room temperature, and of several hours at 0°. Most of the exchange results were obtained with the yellow solution. The effect has been noticed before; Christensen[8] thought it was due to reduction to $Mn(CN)_6^{-4}$ by the free cyanide, an energetically favorable reaction, while Myer[5] supposed the red coloration to be due to small amounts of $Mn(CN)_3$. If an explanation of the first type were correct, namely, that the red form is the actual $Mn(CN)_6^{-3}$ which then undergoes reaction to give an entirely different, yellow species, then the interpretation of any exchange data would be seriously affected. Since Myer did not exhaust alternatives of this nature, it was desirable to study the color change in somewhat more detail than had been done previously.

The absorption spectrum of the yellow solution is given in Fig. 1, and shows a band at 330 mμ as the principal feature, in agreement with a previous report.[9] The spectrum of the

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[1] The work here described was conducted under contract N6 onr 23809 between the University of Southern California and the Office of Naval Research. It was presented in part at the Symposium on "Equilibrium and Rate Behavior of Complex Ions in Solution" held at the University of Chicago, February, 1951.

[2] This paper is in part based on portions of a dissertation submitted by Joan P. Welker in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

[3] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[4] W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 213.

[5] J. Meyer, *Z. anorg. Chem.*, **81**, 385 (1913).

[6] A. W. Adamson, THIS JOURNAL, **69**, 2564 (1947).

[7] The $BaC^{14}O_3$ was obtained from the Isotopes Division of the Atomic Energy Commission.

[8] O. T. Christensen, *J. prakt. Chem.*, **139**, 163 (1885).

[9] L. Szego and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930).

red solution could not be determined as precisely, but, qualitatively, the absorption in the near ultraviolet was very similar, showing the identical peak at 330 mμ. There were, however, new bands at 370 mμ and 510 mμ, but of very much lower optical densities. The retention of the same intensity for the 330 mμ peak suggests that the complex in the red solution is primarily as the yellow form and that the red coloration is due to some minor species. The measurements were made with a Beckman model DU quartz spectrophotometer.

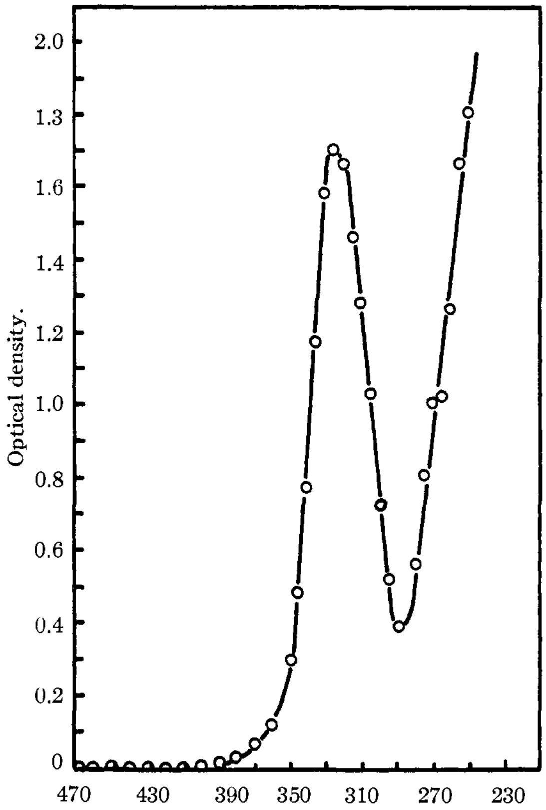

Fig. 1.—Absorption spectrum of $K_3Mn(CN)_6$ (0.000691 *f*) in 0.052 *f* KCN at 3.5° (yellow solution); 1-cm. light path.

During the color change, the *p*H of a solution 0.1 *f* in potassium cyanide and 0.02 *f* in complex rises from 10.9 to 11.3 and the potential at a platinum electrode changes from −0.17 to 0.05 with respect to a saturated calomel reference electrode (the solution becomes less reducing).

Christensen's proposal that the effect was due to reduction to $Mn(CN)_6^{-4}$ was ruled out by performing, in nitrogen atmosphere, a potentiometric titration of the yellow solution with potassium ferricyanide; a change of 0.6 volt should occur at the end-point.[10] Actually, after the first small addition of reagent, no further change in potential took place. Furthermore, the color transition cannot involve any appreciable change in the amount of complexed cyanide as shown by the exchange experiments. Finally, no change in number of unpaired electrons is involved since the paramagnetism of the complex in potassium cyanide solution remained constant, within *ca.* 3% during the change.[11] These findings, plus the spectral evidence suggest that the complex in the yellow solution actually is the hexacyanide of trivalent manganese, and that the initial color is due to the presence of some impurity present in the solid complex, possibly a Mn(III) cyanide of lower coördination number.

One exchange experiment (run "A") was carried out, in duplicate, by dissolving the complex in potassium cyanide solution which had been precooled to 0°, and then adding the potassium radiocyanide solution *immediately*, rather than after the customary half-hour. The exchange time was five minutes.

Experimental Results

The results of a series of exchange experiments at 0° with 0.05 *f* potassium cyanide and 0.02 *f* complex (at the natural *p*H of 10.8), are presented in Table I. The data are plotted in Fig. 2, as ln $y^\infty/(y^\infty - y)$ *vs.* time, where y and y^∞ denote the amount of radiocyanide in the complex, at time t, and at infinite time, respectively. The latter value is computed with the assumptions that all six cyanides exchange and that isotopic mass effects can be neglected. According to the treatment of exchange in a system not undergoing a net reaction, the exchange is first order,[12] and such a plot should yield a straight line of slope, c, equal to $R(1/a + 1/b)$, where a and b are the concentrations of free

TABLE I

RATE OF EXCHANGE OF $KC^{14}N$ WITH $K_3Mn(CN)_6$ AT 0°

Exchange time, min.	Specific activity retained by $KC^{14}N$, %	$\frac{y^\infty}{y^\infty - y}$
$(KC^{14}N) = 0.0596\,f$; $(K_3Mn(CN)_6) = 0.0199\,f$ Ionic strength: 0.18[a]		
5.3	83.7	1.32
10.0	75.4	1.58
15.1	77.9	1.50
20.0	74.9	1.60
48.0	59.9	2.50
64.0	56.7	2.84
80.0	51.4	3.66
120.0	44.0	5.80[b]
5.0 (Run A)[c]	82.7	1.34
$(KC^{14}N = 0.0571\,f$; $(K_3Mn(CN)_6) = 0.0202\,f$ Ionic strength: 1.21[d]		
20.0	78.5	1.46
60.0	55.1	2.94
80.0	52.6	3.30

[a] Estimated ionic strength, assuming complete dissociation of $K_3Mn(CN)_6$ and neglecting any hydrolysis of the complex or of the free cyanide. [b] Carried out in the dark. [c] See Experimental. [d] Ionic strength increased by addition of potassium nitrate.

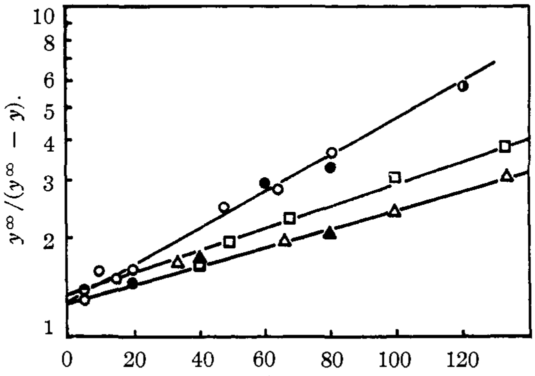

Fig. 2.—Rate of exchange of $K_3Mn(CN)_6$ with KCN in aqueous solution at 0°, 0.0199 *f* $K_3Mn(CN)_6$, 0.0596 *f* KCN: normal runs, ○; dark run, ◑; run "A", ◓; increased μ, ●. [KCN] doubled; normal runs □ [$K_3Mn(CN)_6$] halved: normal runs, △; dark runs, ▲.

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[10] G. Gruber and W. Brause, *Ber.*, **60**, 2273 (1927).

[11] The magnetic measurements were made by Mr. Otto Holecek with the use of a Gouy balance made available by Professor W. K. Wilmarth.

[12] R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946); H. A. C. McKay, *Nature*, **142**, 997 (1938).

cyanide and of cyanide in complex ion, respectively, and R denotes the rate of the reaction responsible for the exchange. The data do fall on a straight line, suggesting that, in fact, no net reaction occurs and, moreover, that a single exchange rate applies to all six cyanides in the complex.

Significance of the Non-zero Intercept.—The line representing the data has a non-zero intercept at zero time corresponding to an amount of exchange equivalent to one-twelfth of a cyanide per manganese. This is probably due to catalysis during separation. The alternative explanation that a continuing net reaction was liberating cyanide is ruled out by the result of experiment A.

The results of run A also preclude the possibility that the red color is due to some different and more labile form of the complex existing transitorily. Since the entire exchange experiment was carried out during the period of existence of the red coloration, the presence of any more exchangeable form would have led to more than the expected amount of exchange.

Prior to the determination of the concentration and temperature dependencies of the exchange rate, several possible sources of complication were explored.

Effect of Light.—As noted in Table I and in Fig. 2, several runs were made in the dark and found to yield the same exchange rate as was observed under ordinary lighting conditions. There was, therefore, no significant photocatalysis.

Effect of Ionic Strength.—As shown in Table I and Fig. 2, there was no effect of increasing the ionic strength from 0.18 to 1.21 (molar concentration units) by means of added potassium nitrate as the inert salt.

Surface Catalysis.—The effect of increased glass surface on the exchange rate is given in Fig. 3, which shows an effect approximately in proportion to the area present. The magnitude was small enough, however, so that no correction was deemed necessary to the exchange data for the runs with the normal area of glass present.

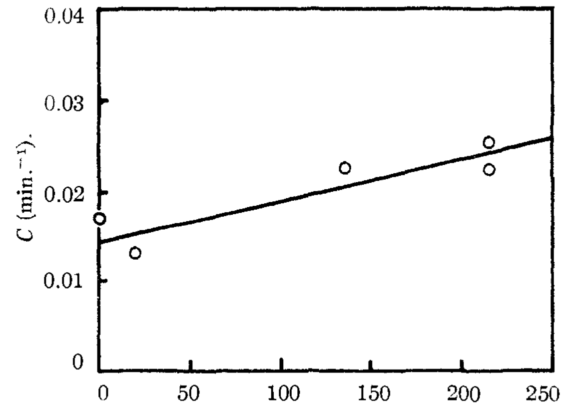

Fig. 3.—Effect of glass surface on the exchange rate at 0°, 0.0199 f $K_3Mn(CN)_6$, 0.0571 f KCN. The point at zero area is for a paraffin lined container; the normal area was 19 cm.^{2}.

This minor surface effect may have been due to some induced decomposition of the complex, yielding MnO_2. This oxide appears to be a catalyst for the exchange since preliminary runs with impure complex (containing MnO_2) yielded much faster exchange rates than those found for the pure complex.

Effect of pH.—The complex was dissolved in potassium cyanide solution already adjusted to the desired pH so as to eliminate local concentration excess. Even so, excessive decomposition occurred with pH's appreciably greater than the natural value of 10.8. It was possible, however, to prepare reasonably stable solutions of pH's as low as 9.0, using perchloric acid as the acidifying agent. It is noteworthy that the velocity of the color change from red to yellow appeared to parallel the degree of instability of the systems toward decomposition.

The data on the variation of exchange rate with pH over the range from 10.8 to 9.0 are plotted in Fig. 4. The values are more erratic than those at the natural pH, due possibly to irreproducible traces of decomposition products acting as catalysts, but indicate no trend in exchange rate over the *ca.* 100-fold range of hydrogen ion concentration that was achieved.

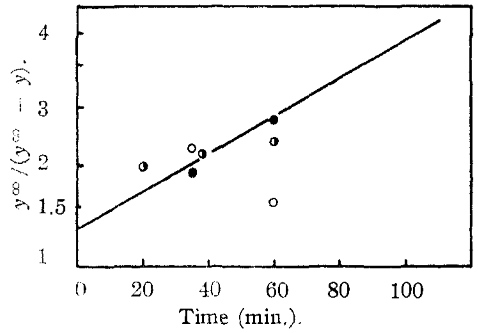

Fig. 4.—Effect of pH on the exchange rate at 0°, 0.0199 f $K_3Mn(CN)_6$, 0.1044 f KCN: heavy line, pH 10.8 (taken from Fig. 2); pH 10.4, ◑; pH 9.9, ●; pH 9.0, ○.

Concentration Dependence of the Exchange Rate.—The effects on the exchange rate of varying the complex and the free cyanide concentrations are presented in Table II and Fig. 2. Columns 3 and 4 of the table give the values of the slopes of the rate plots, c, and of the rate R, of the reaction responsible for the exchange. It is seen that R is nearly independent of the free cyanide concentration, but depends on approximately the first power of the complex concentration. The values of the first order rate constant, k_1, defined by the equation $R = k_1$ (complex), are given in the last column, and are seen to be constant within experimental error. The average value of k_1 is 2.64×10^{-2} min.$^{-1}$; while that of the bimolecu-

TABLE II

CONCENTRATION DEPENDENCE OF THE EXCHANGE AT 0°

Concentration, f Cyanide	Concentration, f Complex	$c \times 10^2$ (min.$^{-1}$)	$R \times 10^4$ (moles liters^{-1} min.$^{-1}$)	$k_1 \times 10^2$ (min.$^{-1}$)
0.0596	0.0199	1.31	5.19	2.61
.0571	.0102	0.865	2.55	2.51
.104	.0199	0.997	5.55	2.79
			Av. k_1	2.64

lar constant, k_2 (see Discussion), is 4.77×10^{-4} mole liters^{-1} min.$^{-1}$.

Temperature Dependence of the Exchange Rate.—The exchange rate was also determined at 10° and at −4°, the latter being the lowest temperature achievable without partial freezing of the solution, and the former, the highest achievable without excessively early initiation of decomposition. The results are given in Fig. 5. The values at 10° are seen to be somewhat erratic; the situation may have been similar to that at the lower *p*H's in that some decomposition of the complex was induced during the handling of the solutions at this higher temperature. The lines drawn for the 10° and the −4° are placed so as to give the maximum activation energy that may reasonably be inferred from the data, since this is desired for the purpose of discussion later. This maximum activation energy is *ca.* 8,500 cal./mole.

Discussion

Certain conclusions may reasonably be drawn regarding the mechanism of this exchange between radiocyanide and the hexacyanomanganate(III) complex. The observation that the exchange rate was essentially independent of ionic strength suggests that there can be only one charged reactant involved in the rate determining step. The concentration dependence studies confirm this in showing the rate to be proportional to the complex ion concentration, but independent of the cyanide concentration. There remains the question of whether it is the unhydrolyzed ion, $Mn(CN)_6^{-3}$ that is the reactant, or some hydrolyzed form such as $HMn(CN)_6^{-2}$ (of the type active in the exchange of ferrocyanide with radiocyanide in solutions of *p*H 3[3]). Since these complexes are fairly strong acids, the concentrations of any hydrolyzed forms should be strongly *p*H-dependent in alkaline solutions, and the lack of *p*H-dependence of the exchange rate, therefore, indicates that the principal reacting form is $Mn(CN)_6^{-3}$.

The above considerations reduce the likely mechanisms to two: monomolecular dissociation, and aquation through a hepta-coördinated transition state.

$$Mn(CN)_6^{-3} \underset{}{\overset{k_1}{\rightleftarrows}} [Mn(CN)_6^{-3}] \rightleftarrows$$
$$Mn(CN)_5^{-2} + CN^- \rightleftarrows \text{etc.} \quad (1)$$
$$R = k_1[Mn(CN)_6^{-3}]$$

$$Mn(CN)_6^{-3} + H_2O \overset{k_2}{\rightleftarrows} [Mn(CN)_6H_2O^{-3}] \rightleftarrows$$
$$Mn(CN)_5H_2O^{-2} + CN^- \quad (2)$$
$$R = k_2[Mn(CN)_6^{-3}][H_2O]$$

Mechanism (1) is unlikely, however, since the unimolecular rate constant, k_1, is much too small in view of the low activation energy. Thus, use of the equation $k_1 = ekT/h\ e^{\Delta S/R}e^{-\Delta E/RT}$ yields the value −44.2 cal./°mole for the standard entropy of activation. Since a maximum value of the activation energy was employed, the magnitude of ΔS is a minimum, and yet even so is much larger than that to be expected for a unimolecular reaction.[13] Entropy values of this order are not uncommon for bimolecular reactions, however, particularly for those involving multi-atomic molecules. Thus, process (2) is the preferred possibility.

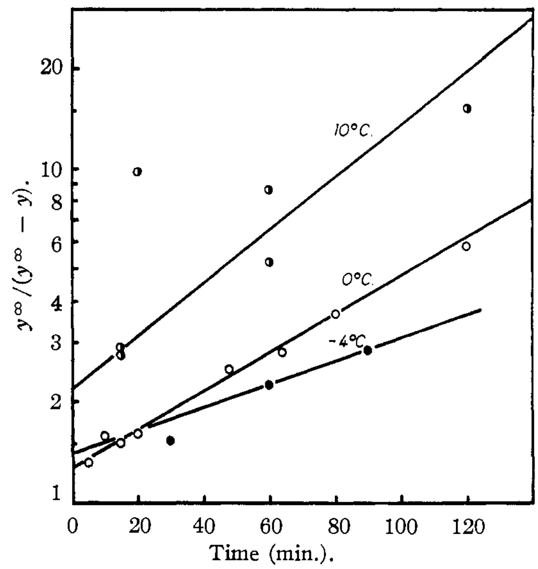

Fig. 5.—Temperature dependence of the exchange: 0.0199 $K_3Mn(CN)_6$, 0.0104 *f* KCN.

It was suggested previously, on the basis of earlier studies with a number of complex cyanides,[3] that a substitution or inversion type of mechanism was more to be anticipated than one involving simple dissociation. The mechanism proposed here is an elaboration of this suggestion in that it is specifically recognized that the coördination number for the transition state must be one greater than that for the normal complex. Such an expansion of the coördination sphere should not be difficult for the tetra-coördinated cyanides; thus $Ni(CN)_4^{-2}$ has available an unfilled 4*p* orbital which can accommodate a fifth cyanide or other group, and provide a path for the observed immeasurably rapid exchange. The same argument applies to $Pd(CN)_4^{-2}$ for which the exchange was also immeasurably rapid.

Exchange with hexacyanides by this mechanism, involves an increase in coördination number to seven. The nature of the directed orbitals in such a case has not been very fully considered. Kimball[14] has supposed that *f* orbitals are involved, but, for simplicity, both he and Duffy[15] have made use of d^3sp^3 hybridization in discussing the structures of ZrF_7^{-3} and IF_7. It is much more likely, for first row transition elements at least, that expansion from the d^2sp^3 octahedral configuration into an additional *d* orbital should occur rather than into an energetically less favorable *f* orbital. Even so, the process should be improbable for the hexacyanides of cobalt and iron since one or two electrons would have to be promoted to the next shell. On the other hand, the increase in coördination number should more easily be possible for $Cr(CN)_6^{-3}$ and might well be somewhat stabilized in the case of $Mn(CN)_6^{-3}$ by the fact that the resulting hepta-coördinated complex would, in the latter instance, have a "rare gas" structure. This

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[13] See S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 296.

[14] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[15] G. H. Duffy, *ibid.*, **18**, 943 (1950).

reasoning accounts qualitatively for the observed order of increasing lability toward exchange with radiocyanide: $Co(CN)_6^{-3} \sim Fe(CN)_6^{-3} < Cr(CN)_6^{-3} \ll Mn(CN)_6^{-3}$.

One additional point should be considered, namely, why the exchange should proceed through a hepta-coördinated complex with water rather than with cyanide as the seventh group. The answer may lie in the known reluctance of similarly charged ions to react and in the high concentration of water as compared to cyanide ion. As a means of extending this and other aspects of the picture, it will be of interest to examine the kinetics of the exchange of radiocyanide with $Cr(CN)_6^{-3}$; the exchange rates for the iron and cobalt complexes appear to be too slow to permit quantitative study.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 5, 1951

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. XI. Side Chain Reactions of Furfural and Furfuryl Alcohol over Nickel–Copper and Iron–Copper Catalysts[1]

BY ROBERT M. LUKES AND CHRISTOPHER L. WILSON

The reactions of furfural and furfuryl alcohol in the presence of hydrogen have been studied over catalysts containing nickel–copper and iron–copper mixtures at atmospheric pressure and elevated temperatures. Furfural is reduced to furfuryl alcohol most effectively using nickel–copper catalysts although the 10 iron–90 copper was also fairly good. The best yield (97%) was obtained at 110° with 80 nickel–20 copper. Pure copper was useless. Over 200° the chief reaction was the formation of furan and again the nickel–copper catalysts were best, the highest yield (46%) being afforded by 50 nickel–50 copper. In the iron series that containing 10 iron–90 copper was best but the product also contained much methylfuran. Pure copper again had no activity.

Furfuryl alcohol reacted best over the iron–copper catalysts to give methylfuran. With 10 iron–90 copper the yield was 80%. The nickel materials were very poor and copper again inactive. On the basis of the results the best catalyst for the direct conversion of furfural into methylfuran should be that containing 10 iron–90 copper. Experiments at 250° gave 25% yield. The reactions are discussed in relation to the view that catalysis in hydrogenation, hydrogenolysis and decarbonylation is facilitated by the presence of unfilled 3*d*-electron levels in the catalytic metals.

Earlier in this series[2] the formation of furan and methylfuran from furfural using nickel- or cobalt-containing catalysts was described. Under optimum conditions with a 44 nickel–56 copper catalyst at 280–290°, the yield of furan was over 60%. These preliminary results have now been extended using sintered metal powder catalysts[3] consisting of 100 nickel, nickel–copper mixtures with 80 and 50 nickel, and iron–copper mixtures with 96, 50 and 10 iron. Since all reduction experiments with furfural indicate that the first product is always furfuryl alcohol, this substance has also been studied in order to unravel the reaction steps. The temperature range 100–400° has been covered. Below 200°, not investigated earlier,[2] reactants and products were essentially liquid since all experiments were carried out at atmospheric pressure; above this point they were mainly vapors. The change of state did not result in any pronounced discontinuity of catalytic result as can be seen from Figs. 2, 3 and 4, but large changes of temperature did do so. Hydrogen was added to the input in all experiments since experience has shown that even in reactions such as side chain elimination, in which hydrogen is not used up, its presence is essential to prevent rapid deterioration of the catalyst. With each catalyst, the effect of changing temperature on the products was determined by carrying out a series of consecutive experiments without reactivating the catalyst. The last experiments in each series were made at the temperatures of the first ones in order to determine the extent of catalyst deterioration. Only when this was slight or negligible were the data acceptable. One such suitable set of experiments is given at the end of the experimental section.

The main reaction paths are indicated in Fig. 1. Reduction (a) has been fairly extensively studied before but little has been done systematically to determine the relationship between nature of the catalyst and progress of reaction. This is now remedied in part. The double arrow (a and c) between the aldehyde and the alcohol does not necessarily imply equilibrium, but merely that the reaction may proceed in either direction depending on conditions. In the present experiments, a flow technique was employed and equilibrium was not attained.

Reduction of Furfural to Furfuryl Alcohol (reaction (a), Fig. 1).—Almost any hydrogenation catalyst will reduce furfural to the alcohol although industrially a copper catalyst is preferred since it does not favor nuclear reduction even at high pressure. The temperature is preferably below 200° since above this point hydrogenolysis to methylfuran supervenes. Unsupported copper is inactive but becomes effective when carried on a material such as asbestos,[4] kieselguhr,[5] active carbon[5] or zinc oxide containing sodium carbonate.[6] Raney copper[7] or cuprous oxide supported

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(1) A summary was read before the Organic Division of the American Chemical Society in Philadelphia, April, 1950; Previous paper in this series, THIS JOURNAL, **70**, 1313 (1948).

(2) Wilson, *J. Chem. Soc.*, 61 (1945); Boles, Hungarian Patent 132,763 (1944); *C. A.*, **43**, 4301 (1949).

(3) Wilson, THIS JOURNAL, **70**, 1312 (1948).

(4) Brown, Gilman and Van Peursem, *Iowa State Coll. J. Sci.*, **6**, 133 (1932).

(5) Burnette, *ibid.*, **19**, 9 (1944); Katsuno, *J. Soc. Chem. Ind. Japan*, **46**, 859 (1943); *C. A.*, **43**, 1719 (1949).

(6) Graves (to du Pont), U. S. Patent 2,077,409 (1937); *C. A.*, **31**, 3964 (1951).

(7) Mizuguchi and Iwase, *J. Soc. Chem. Ind. Japan*, **46**, 1037 (1943); *C. A.*, **42**, 6353 (1948).