permit a definite choice of one mechanism over the other for the formation of cyclohexyl cyanide.

The yields of hydrogen, cyclohexene, and dicyclohexyl were reduced in the presence of cyanogen, and the yields of all the minor products showed some decrease with increasing concentration of cyanogen. The hydrocarbon radiolysis products from the cyanogen–cyclohexane mixtures were qualitatively the same as those from pure cyclohexane except for unknowns 2 and 3, which were not detected as products in the mixtures. The yield of hydrogen decreased with increasing concentration of cyanogen up to approximately 0.1 M and appeared to have reached a limiting value of $G \sim 4$ at the higher concentrations. Other substances, such as cyclohexane,[1,2] benzene,[3,5,10] iodine,[5,7-9] carbon tetrachloride,[12] and chloroform,[12] also decrease the hydrogen yield by varying amounts. Hydrogen is generally considered to be produced simultaneously by a unimolecular process and a bimolecular process[1,5]; a third undefined process also has been suggested to account for a portion of the hydrogen.[2] Even though a number of investigations have been devoted to the effects of solutes on the hydrogen yield from cyclohexane, the processes have not been completely elucidated. The effects of solutes have been attributed to H-atom scavenging, electron attachment, energy transfer, and quenching. From the available data, cyanogen is the least efficient of the various solutes in decreasing the hydrogen yield, being slightly less efficient than benzene[10] and cyclohexene.[4] The similarity of the results from this work with those from γ-irradiated benzene–cyclohexane mixtures and carbon tetrachloride–cyclohexane mixtures suggests that the effect of cyanogen may be of the same nature as that suggested for benzene[10] and carbon tetrachloride.[12]

The yield of cyclohexene showed a rapid decrease to $G = 1.58$ at 0.067 M and then a more gradual decrease with increasing concentration to $G = 1.25$ at 0.268 M. The dicyclohexyl yield decreased sharply to $G = 0.42$ at 0.067 M and then decreased only slightly to $G \sim 0.38$ at the higher concentrations. The effect of cyanogen in decreasing the yields of cyclohexene and dicyclohexyl is very similar to the effects of benzene[10] and chlorinated solutes,[12] with the yields of cyclohexene agreeing with those from chloroform–cyclohexane solutions and with the yields of dicyclohexyl agreeing with those from cyclohexane solutions of chloroform and carbon tetrachloride. The efficiencies of the different solutes vary, and for each solute there are residual yields of cyclohexene and dicyclohexyl. The formation of cyclohexene has been attributed to the disproportionation of cyclohexyl radicals and to the unimolecular decomposition of some form of the excited cyclohexane mole-

cule; the formation of dicyclohexyl has been attributed to the combination of cyclohexyl radicals.[1] In addition, other modes of formation for cyclohexene and dicyclohexyl have been suggested.[2,12] A portion of the decrease in the yields of cyclohexene and dicyclohexyl can be ascribed to the radical scavenging action of the solute; in this case, cyanogen or a polymeric form of cyanogen. For cyclohexene, a part of the decrease has been attributed to interaction of the solute with some form of an excited cyclohexane molecule, thereby preventing its unimolecular decomposition to hydrogen and cyclohexene.[12] Since the yields of cyclohexene from cyanogen–cyclohexane solutions are in agreement with the yields reported for the solutes, chloroform and carbon tetrachloride,[12] the cyanogen could interact in a similar manner. The residual yields of cyclohexene and dicyclohexyl in the presence of cyanogen may be due to chain termination steps and/or to reactions of cyclohexyl radicals in the same solvent cage. If cyclohexyl cyanide is formed in a chain process as suggested above, then the disproportionation and combination of cyclohexyl radicals would constitute two chain termination steps to yield cyclohexene and dicyclohexyl. As suggested by Hardwick,[18] some or all of the yields of cyclohexene and dicyclohexyl at the higher concentrations of solute may be due to the disproportionation and combination reactions of the cyclohexyl radicals formed together in the same solvent cage.

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Activity Coefficients of Cadmium Chloride in Mixed Aqueous Solution with Benzyltrimethylammonium Chloride[1]

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Because of an anticipated need for such data in connection with another project, activity coefficients were determined for cadmium chloride in aqueous solutions

with benzyltrimethylammonium chloride by the e.m.f. method at total stoichiometric ionic strengths of 1.0, 0.5, and 0.2 m. These were the ionic strengths used by Leifer, Argersinger, and Davidson[2] in determining the activity coefficients of both cadmium chloride and hydrochloric acid in mixed aqueous solutions. Harned and Gary[3] had earlier reported the activity coefficients of hydrochloric acid in cadmium chloride solutions of total stoichiometric ionic strength of 5.0.

Experimental

A concentrated stock solution of cadmium chloride was prepared from Baker's Analyzed reagent and deionized water. Standardization was by gravimetric determination of cadmium as sulfate and was verified by gravimetric determination of chloride. The stock solution of benzyltrimethylammonium chloride was Matheson 60% aqueous solution and was standardized by gravimetric determination of chloride. Mixed solutions of stoichiometric ionic strength of 1.0 m were prepared from the stock solutions, using weight burets. Portions of the 1.0 m solutions were deoxygenated by bubbling of nitrogen under reduced pressure and were transferred to flushed e.m.f. cells with nitrogen pressure. Solution compositions in the prepared cells were corrected for loss of water.

The e.m.f. cell used may be represented by

$$CdHg_x \,|\, CdCl_2(m_2),\ C_{10}H_{16}NCl(m_1)\ |AgCl-Ag$$
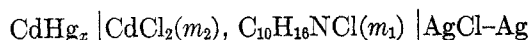
The cadmium amalgam, approximately 8% cadmium by weight, was prepared, stored, and transferred to the cells under nitrogen. The silver–silver chloride electrodes were prepared by the thermal method.[4] The standard potentials used were 0.35163 and -0.22246 abs. v., respectively. Cell measurements were made with a Leeds and Northrup Type K-3 potentiometer in conjunction with an electronic null indicator. Cells were made up in triplicate and were kept at $25 \pm 0.05°$ during the measurements. Deviations from the average of triplicate measurements were of the order of 0.05, 0.1, and 0.2 mv. for ionic strengths 1.0, 0.5, and 0.2, respectively, except that for small X_2 at 0.2 m ionic strength, deviations >0.5 mv. were obtained for some cells.

Results

The results of the cell measurements are recorded in Table I, along with the calculated values of the logarithms of the stoichiometric mean ionic activity coefficients of cadmium chloride in the solutions. The latter have been adjusted by short interpolation to the

appropriate ionic strength in cases where the ionic strength differed significantly from its intended value.

Table I: Cell Measurements and Calculated Activity Coefficients of $CdCl_2$

Total stoichiometric ionic strength, $I = 3m_2 + m_1$	Ionic strength fraction of $CdCl_2$, $X_2 = \dfrac{3m_2}{I}$	Measured cell potential, E, in abs. v.	$-\log \gamma_2$
1.0063	0.09969	0.70800	1.006
0.9882	0.19805	0.69851	0.989
1.0072	0.3020	0.69222	0.967
0.9985	0.3951	0.68855	0.955
1.0000	0.4998	0.68510	0.939
1.0010	0.5991	0.68269	0.926
0.9935	0.6997	0.68052	0.911
1.0119	0.8064	0.67936	0.905
0.9991	0.9002	0.67896	0.904
1.0000	1.0000	0.67906	0.905
0.5093	0.09969	0.71407	0.778
0.4877	0.19805	0.70664	0.774
0.5052	0.3020	0.70185	0.778
0.4992	0.3951	0.69870	0.768
0.5000	0.4998	0.69620	0.763
0.5002	0.5991	0.69412	0.754
0.5235	0.6997	0.69192	0.752
0.5002	0.8064	0.69200	0.747
0.4995	0.9002	0.69185	0.748
0.5002	1.0000	0.69180	0.749
0.2004	0.09969	0.73235	0.582
0.1999	0.19805	0.72391	0.576
0.1998	0.3020	0.71945	0.577
0.2003	0.3951	0.71707	0.579
0.1999	0.4998	0.71510	0.578
0.2000	0.5991	0.71308	0.570
0.1992	0.6997	0.71249	0.571
0.1973	0.8064	0.71214	0.569
0.2001	0.9002	0.71113	0.568
0.2001	1.0000	0.71110	0.569

The effect of benzyltrimethylammonium chloride on the activity coefficient of cadmium chloride is considerably different from that of hydrochloric acid in solutions of analogous composition,[2] particularly at the higher solution concentrations. This behavior could be of some interest because of the relationship of benzyltrimethylammonium chloride to the common type of anion-exchange resin, although the concentrations of the quaternary ammonium ion within these resins usually are much higher than those recorded here.

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(3) H. S. Harned and R. Gary, *ibid.*, **63**, 2086 (1959).

(4) D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press, New York, N. Y., 1961, Chapter 4.