Kinetics of Sulfochlorination of Cyclohexane in Carbon Tetrachloride Induced by Gamma Radiation

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Solutions of cyclohexane, chlorine, and sulfur dioxide in carbon tetrachloride were irradiated in an oxygen-free system with gamma rays from uranium fission products contained in spent fuel elements. Reaction rates, equivalent to the rate of disappearance of free chlorine, were determined spectrophotometrically at 4,000Å. The reaction products were cyclohexanesulfonyl chloride and hydrochloric acid in nearly stoichiometric quantities. An empirical rate equation was derived, in which the rate of disappearance of chlorine was shown to be proportional to the square root of the product of absorbed radiation, chlorine and cyclohexane concentrations, and independent of the concentration of sulfur dioxide. A chain mechanism was proposed, and the rate equation derived from this scheme was found to be in excellent agreement with the empirical rate equation. The reaction proceeded by a free radical mechanism, as evidenced by the strong inhibiting effect of oxygen. G numbers were of the order of 10^5, corresponding to an estimated chain length of 5,000, which is of the same order as the quantum yield of the photochemical sulfochlorination.

There has been growing interest in the study of radiation processing in recent years (*1, 4, 5, 6, 10, 13, 15, 16*) with special emphasis given to exploring its industrial application (*11, 12, 13, 17*). One of the outstanding examples is the direct sulfochlorination of cyclohexane in the presence of gamma radiation.

The direct sulfochlorination of cyclohexane by reaction with sulfur dioxide and chlorine in the presence of gamma radiation was studied in detail (*13*). For sulfur dioxide/chlorine ratios in the feed gas exceeding 1, cyclohexanesulfonyl chloride was the major product, while the chlorination product, cyclohexane chloride, formed only to a small extent.

The objective of this study was the investigation of the kinetics of the sulfochlorination of cyclohexane dissolved in carbon tetrachloride, particularly the effect of such variables as concentration of reactants and radiation intensity on the reaction rates. Under certain circumstances, kinetics data can be used to explain the mechanism of a reaction, particularly in the case of a chain reaction. The postulation of a reaction mechanism formed another objective of the kinetics study of the sulfochlorination of cyclohexane.

EXPERIMENTAL PROCEDURE

Reaction rates were determined for dilute solutions of cyclohexane in carbon tetrachloride with a batch reactor. Carbon tetrachloride was selected as the solvent because of the good solubility in it of all reactants, particularly chlorine and sulfur dioxide, and its chemical (but not radiochemical) inertness. The equipment used in these studies is shown schematically in Figure 1.

Before proceeding with the measurement of reaction rates, it was necessary to confirm the stoichiometric validity of the proposed overall reaction, namely

$$C_6H_{12} + SO_2 + Cl_2 \rightarrow C_6H_{11}SO_2Cl + HCl \qquad (1)$$

Fifty milliliters of a solution of cyclohexane in carbon tetrachloride containing a carefully measured quantity of cyclohexane were introduced into the spherical reservoir of the inverted reactor (reservoir at bottom). With water of 1°C. circulating through the outer jacket, the air was evacuated from the reactor and supply lines, until the liquid started to flash. The system was then filled with argon, and the inert gas was swept through the supply lines for 5 min. This was repeated several times, the reactor being finally filled with argon to a pressure of 5 lb./sq.in. gauge. A sample was withdrawn and the actual cyclohexane content obtained from a refractive index determination. It was found that repeated flashings did not noticeably alter the cyclohexane content, since cyclohexane and carbon tetrachloride have very similar vapor pressure curves, and the vapor- and liquid-phase compositions are quite close for this binary system (*7*). The gas supply valve was closed, and the reactor was inverted to its normal position with a bulb on top. This bulb acted as a reservoir during sampling. It was not filled with liquid during irradiation. The gas metering loop and the supply lines were evacuated to less than 1 mm. mercury; an exact quantity of chlorine was metered out from the metal loop with the aid of a calibrated pressure gauge and the system filled with argon to maintain a constant pressure of 5 lb./sq.in. gauge. This gas mixture was then bubbled through the liquid in the reactor maintained at 1° to 3°C. for exactly 10 min., at a rate of 80 to 100 bubbles/min. Under these conditions, the gas absorption was found to be quantitative. Sulfur dioxide was introduced in a similar manner. The amounts of gas supplied were obtained from the pressure decrease in the respective metering loops. To verify the accuracy of this procedure, the sulfur dioxide content was determined chemically (ex-

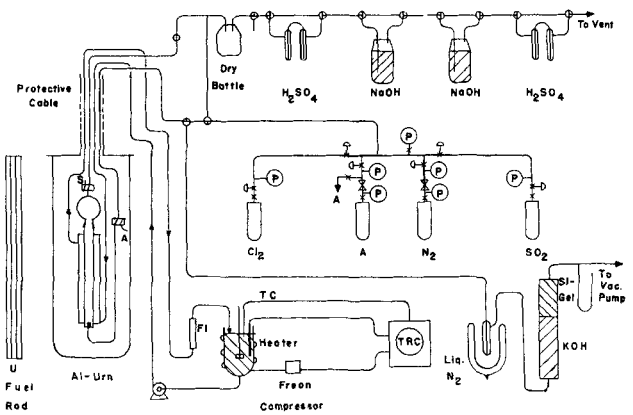

Fig. 1. Apparatus for kinetics studies.

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tracted carbon tetrachloride solution with 2.5% ammonia, added hydrogen peroxide to oxidize sulfite to sulfate, boiled to remove excess ammonia and to decompose unreacted hydrogen peroxide and then titrated with barium chloride, with a THQ indicator). The chlorine content was found spectroscopically and also chemically (extracted with 2.5% ammonia, boiled to convert any ammonium hypochlorite present into ammonium chloride, titrated with silver nitrate at a pH of 7.0, with fluorescein as an indicator). Following a short irradiation, the liquid was removed from the reactor, and the various ingredients were determined as follows:

chlorine—spectroscopically

chlorine, hydrochloric acid, sulfur dioxide—flashed over and absorbed in 2.5% ammonia, boiled and determined chloride ion and sulfate ion as above. Hydrochloric acid obtained by difference

cyclohexanesulfonyl chloride—weighed as residue after distilling off cyclohexane and carbon tetrachloride at reduced pressure (10 to 15 mm. Hg).

The results of four determinations showed good agreement with Equation (1). An average of 0.93 mole cyclohexanesulfonyl chloride was formed by the disappearance of 1 mole of chlorine.

The rate of disappearance of chlorine from carbon tetrachloride solution was conveniently measured with a spectrophotometer at 4,000Å. At this wave length, chlorine was the only strongly absorbing substance in the system. A calibration curve for the optical density of chlorine in carbon tetrachloride at 4,000Å was obtained by extracting the carbon tetrachloride solutions with 2.5% NH_3, boiling the extract and titrating with silver nitrate to determine the chloride ion content with a fluorescein indicator.

All irradiations were performed in the Argonne High-Level Gamma Irradiation Facility. The radiation source consisted of spent fuel elements, containing a large number of highly radioactive elements from the fission of enriched uranium. The irradiation facility and the equipment used in the sulfochlorination studies have been described in detail elsewhere (*13*).

After the reactants were charged as described above, the temperature of the circulating water was raised to the desired point, and the reactor was lowered into the irradiation rack for varying lengths of time (usually 1 min.). Following the irradiation period, the urn and reactor were brought up to withdraw a 4-ml. sample. The system was maintained at constant pressure (5 lb./sq.in. gauge) during irradiation and sampling, by means of argon gas supplied through a pressure reducing valve.

Before sampling, the inverted reactor was thoroughly agitated to ensure uniformity. The irradiations were repeated two to four times, until the chlorine concentration became sufficiently low. At first, special precautions were taken to prevent a change of chlorine concentrations in the sample by a photochemical reaction, but it appeared that after the contact with air the chlorine concentration remained unchanged, even when exposed to ordinary room illumination for longer periods of time.

It was noted that immediately following the charging of the gases, the chlorine concentration decreased slightly. This was probably due to the formation of small amounts of sulfuryl chloride and some loss of the dissolved chlorine by evaporation into the surrounding argon gas. In the temperature range studied, sulfochlorination does not occur without initiation by light, radiation, or catalysts, but, for convenience, the overall decrease in the concentration of chlorine not due to irradiation will be designated as *dark reaction.*

The experimentally determined rate of the dark reaction can be expressed by

$$-\frac{\Delta(Cl_2)}{\Delta t} = 0.03 \times 10^{-3}\,(Cl_2) - 1.1 \times 10^{-3} \qquad (2)$$

The decrease in chlorine concentration due to the dark reaction was deducted from the overall difference between two consecutive samplings to obtain the net consumption of chlorine due to irradiation.

The variables studied in the course of this study were chlorine, sulfur dioxide, and cyclohexane concentrations, and the intensity of the gamma radiation at a constant temperature of 25°C. In addition, in one run the solution was saturated with oxygen prior to irradiation.

EXPERIMENTAL RESULTS

The experimental results, not corrected for the dark reaction, are shown in Figure 2.

The average rates were calculated for each interval between samplings and correlated with the average concentration of the reactants during this period. This apparent reaction rate was corrected for the loss of chlorine by a dark reaction. In calculating the absorbed gamma dose, empirically determined factors were used to correct for variation in the volume occupied by the liquid in the reactor. The ratio of the electron densities for cyclohexane and carbon tetrachloride mixtures and that of water was used to convert from rad (water), obtained from the Fricke dosimeter, to rad (solution) for the same flux. The log of the calculated reaction rates were then plotted (Figures 3 and 4) against the log of the corresponding chlorine concentrations, with cyclohexane concentrations and gamma radiation intensities, respectively, as parameters. The effect of these two parameters on the reaction rate is shown in Figures 5 and 6, which were constructed by cross plotting the corresponding rates from the two preceding graphs. These graphs were then used to derive the following empirical rate equation:

$$-\frac{\Delta(Cl_2)}{\Delta t} = 1.08\,\frac{\Delta(C_6H_{11}SO_2Cl)}{\Delta t} = K\sqrt{I(Cl_2)\,(C_6H_{12})} \qquad (3)$$

The average of all calculated reaction velocity constants at 25°C. is

$$K_{25} = 0.0154 \pm 0.000666\ (\text{min.})^{-0.5}\ (\text{rad.})^{-0.5}$$

The indicated limits are for the 95% confidence level.

The reaction was almost completely inhibited by oxygen and doubling the concentration of sulfur dioxide did not affect the reaction rate.

DISCUSSION OF RESULTS

The great rapidity with which the sulfochlorination of cyclohexane in carbon tetrachloride was found to proceed when initiated by gamma radiation immediately suggested a chemical chain reaction of considerable chain length. Such a chain reaction has been previously postulated for the photochemical sulfochlorination of aliphatic and cycloaliphatic hydrocarbons. The strong inhibiting action of

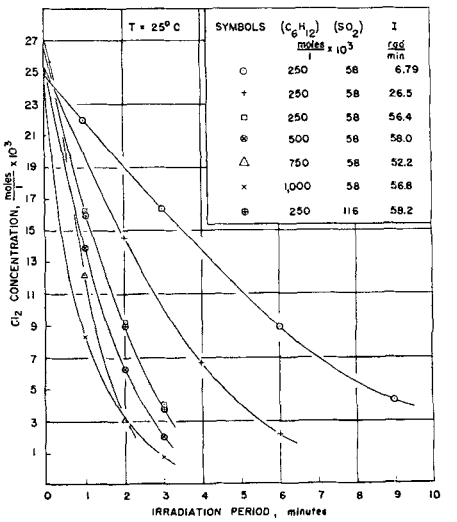

Fig. 2. Sulfochlorination of cyclohexane in carbon tetrachloride.

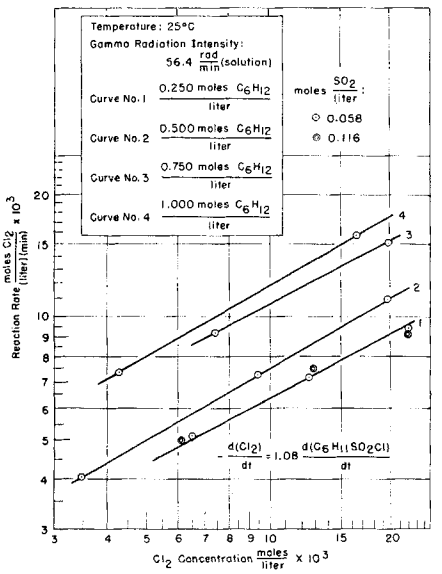

Fig. 3. Effect of chlorine and cyclohexane concentrations on sulfochlorination rate of cyclohexane.

oxygen also supports a free radical mechanism of this reaction.

Kharasch and co-workers (*10*) proposed the following equation for the rate of the photochemical reaction:

$$-\frac{d(Cl_2)}{dt} = k_2'\sqrt{\frac{2I_{abs}}{k_5'}}\,(RH) \qquad (4)$$

Indeed, Stauff (*14*) has found that the photochemical sulfochlorination of heptane and hexadecane in carbon tetrachloride conforms to the following empirical rate equation:

$$-\frac{\Delta Cl_2}{\Delta t} = K'\sqrt{I_{abs}}\,(RH) \qquad (5)$$

The rate equation derived in the present investigation for the gamma-induced sulfochlorination differs from the above. This is not surprising if one considers that the photochemical reaction must be initiated by the dissociation of a chlorine molecule, since in the range of the spectrum in which the reaction was carried out (4,360Å) chlorine is the only component with a strong absorption band.

The interaction of gamma radiation with matter leads to the production of excited molecules or atoms, which are capable of initiating chemical reactions in a manner generally associated with free radicals.

In the present system, the concentrations of chlorine and sulfur dioxide were quite low, making it unlikely that any appreciable number of primary initiating free radicals originate from these components. Both cyclohexane and carbon tetrachloride are known to produce free radicals under gamma irradiation (*4*). The number of free radicals formed were estimated by scavenging them with diphenylpicrylhydrazyl or by initiating the polymerization of styrene and determining the number of polymer chains thus formed. These results indicate that the number of free radicals produced by irradiating carbon tetrachloride is at least three times the number of free radicals from the radiolysis of cyclohexane. Other investigators (*18*) have measured the free chlorine produced during the irradiation of pure carbon tetrachloride.

The numerical results from both studies will be used in calculating the average chain length of the gamma-induced sulfochlorination of cyclohexane. If one further considers that there were ten to forty times as many carbon tetrachloride as there were cyclohexane molecules in the irradiated solution, it follows that the number of free radicals produced by the radiolysis of carbon tetrachloride exceeds by far those originating from the radiolysis of cyclohexane. Consequently, in the proposed reaction mechanism it will be assumed that the chain reaction is initiated by free radicals from carbon tetrachloride. The excellent agreement between the reaction rate equation derived from the proposed mechanism scheme and that arrived at by correlating the experimental data is an indirect proof for the correctness of the postulated mechanism.

THE MECHANISM OF THE DIRECT SULFOCHLORINATION OF CYCLOHEXANE IN CARBON TETRACHLORIDE

Overall reaction:

$$C_6H_{12} + SO_2 + Cl_2 = C_6H_{11}SO_2Cl + HCl$$

Rate equation derived from experimental data:

$$-\frac{d(Cl_2)}{dt} = K\sqrt{I\,(Cl_2)\,(C_6H_{12})}$$

Proposed mechanism:

Initiation—$CCl_4 \rightarrow CCl_3\cdot + Cl\cdot$

Propagation—$C_6H_{12} + Cl\cdot \rightarrow C_6H_{11}\cdot + HCl$

$C_6H_{11}\cdot + SO_2 \rightarrow C_6H_{11}SO_2\cdot$

$C_6H_{11}SO_2\cdot + Cl_2 \rightarrow C_6H_{11}SO_2Cl + Cl\cdot$

Termination—$C_6H_{11}SO_2\cdot + Cl\cdot \rightarrow C_6H_{11}SO_2Cl$

$2CCl_3\cdot \rightarrow C_2Cl_6$

$$-\frac{d(Cl_2)}{dt} = k_4\,(C_6H_{11}SO_2\cdot)\,(Cl_2) \qquad (6)$$

$$\frac{d(C_6H_{11}SO_2\cdot)}{dt} = k_3\,(C_6H_{11}\cdot)\,(SO_2) - k_4\,(C_6H_{11}SO_2\cdot)\,(Cl_2) - k_5\,(C_6H_{11}SO_2\cdot)\,(Cl\cdot) \qquad (7)$$

$$\frac{d(Cl\cdot)}{dt} = 2I - k_2\,(C_6H_{12})\,(Cl\cdot) + k_4\,(C_6H_{11}SO_2\cdot)\,(Cl_2) - k_5\,(C_6H_{11}SO_2\cdot)\,(Cl\cdot) \qquad (8)$$

$$\frac{d(C_6H_{11}\cdot)}{dt} = k_2\,(C_6H_{12})\,(Cl\cdot) - k_3\,(C_6H_{11}\cdot)\,(SO_2) \qquad (9)$$

For steady state conditions the rates given by Equations (7), (8), and (9) are all zero.

By solving the previous equations and assuming that $\frac{I}{2}$ and $\frac{I^2}{4}$ terms are small compared with the other term, one obtains the equation for the disappearance rate of chlorine:

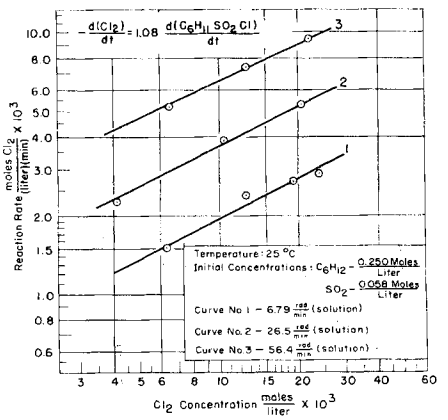

Fig. 4. Effect of chlorine concentration and gamma radiation intensity on sulfochlorination rate of cyclohexane.

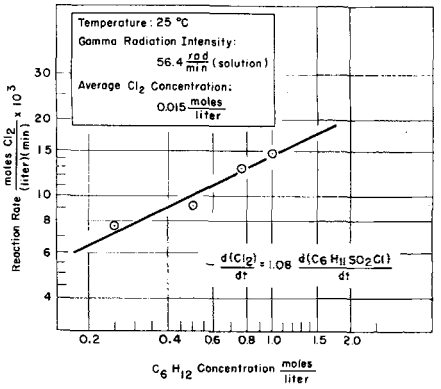

Fig. 5. Effect of cyclohexane concentration on sulfochlorination rate of cyclohexane.

$$\frac{d(Cl_2)}{dt} = \sqrt{\frac{k_2 k_4}{k_5} I (Cl_2)(C_6H_{12})} \qquad (10)$$

Equation (9), as derived from the proposed mechanism for the chain reaction, is identical with the empirical equation if the equality

$$K = \sqrt{\frac{k_2 k_4}{k_5}} \qquad (11)$$

is made.

RADIOCHEMICAL YIELDS AND CHAIN LENGTHS

The G number for the consumption of chlorine is numerically equal to the G number for the production of cyclohexanesulfonyl chloride multiplied by 1.08:

$$-G_{Cl_2} = 1.08\, G_{C_6H_{11}SO_2Cl}$$

Experimental conditions:

(Cl_2) = 0.015 mole/liter
(C_6H_{12}) = 0.250 mole/liter
(SO_2) = 0.048 mole/liter
I = 50 rad. (solution)/min.

Density of solution:

1.56 g./cc. at 25 deg.

Reaction rate:

$$-\frac{d(Cl_2)}{dt} = 4.09 \times 10^{21} \frac{\text{molecules}}{(\text{liter})(\text{min.})}$$

The yield shown above converts to

$$1.18 \times 10^4 \frac{\text{lb.}}{\text{kw.-hr.}}$$

It is interesting to note that, even though the concentrations for this yield calculation were taken arbitrarily, and are obviously not optimum values, the yield of

$$1.18 \times 10^4 \text{ lb./kw. hr.}$$

ranks with some of the highest radiochemical yields reported to date, as shown in the following table:

Reaction	lb./kw. hr.	Ref.
$C_6S_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$	1×10^5	(9)
Polymerization of N-vinyl-pyrollidone in water	2.2×10^4	(2)
Polymerization of acrylonitrile in water (with X-rays)	5×10^5	(3)

The average chain length m, expressed as molecules of

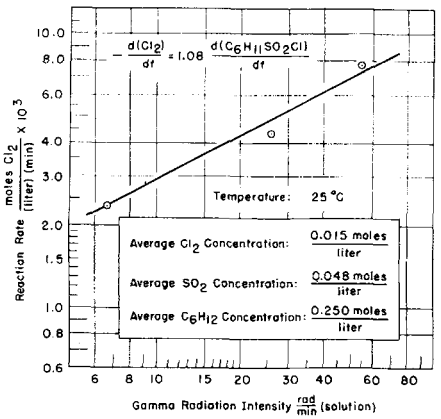

Fig. 6. Effect of gamma radiation intensity on sulfochlorination rate of cyclohexane.

product formed per initiating free radical, is obtained from the respective G numbers; thus

$$m = \frac{G_{C_6H_{11}SO_2Cl}}{G_R}$$

Since the two published values for the G_R of carbon tetrachloride were obtained by different methods, the values differ somewhat. The G_R determined with DPPH (4) is 18.4, while the G_R calculated from the amount of free chlorine generated by gamma irradiation (18) is 14.2:

$$m_1 = \frac{8.40 \times 10^4}{18.4} = 4.57 \times 10^3$$

and

$$m_2 = \frac{8.40 \times 10^4}{14.2} = 5.91 \times 10^3$$

Thus

$$\bar{m} = 5.24 \times 10^3$$

This value compares quite well with the quantum yield of 5×10^3 reported for the photochemical sulfochlorination of hydrocarbons (8).

Stauff (14) reported a quantum yield for the photochemical sulfochlorination of heptane of 3.5×10^4 for the following concentrations:

(C_7H_{14}) — 0.5 mole/liter
(Cl_2) — 0.05 mole/liter
(SO_2) — 0.05 mole/liter

If the chain length determined in this study is recalculated for the above concentrations with the aid of the empirical rate equation, there is obtained a value for m of 1.34×10^4, which is of the same order of magnitude as the photochemical quantum yield.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the Argonne National Laboratory, the interest of Stephen Lawroski and H. Gladys Swope in this work, and the assistance of Ernest King, Kasis Almenas, and Peter Martin, in obtaining some of the data.

NOTATION

A,B = constants
(Cl_2) = concentration of chlorine, moles/liter
(C_6H_{12}) = concentration of cyclohexane, moles/liter
$(C_6H_{12}SO_2Cl)$ = concentration of cyclohexanesulfonyl chloride, moles/liter
I = absorbed gamma energy, rad./min.
I_{abs} = absorbed light energy
K = reaction velocity constant, $(\text{min.})^{-0.5}$ $(\text{rad.})^{-0.5}$
k_2, k_3, k_4, k_5 = reaction velocity constant as appeared in Equations (6 to 11)

k_2', k_5, K' = reaction velocity constants for photochemical reactions, consistent units

$m, m_1, m_2, \bar{m}$ = average chain length, that is number of molecules per initiating free radical

(RH) = concentration of hydrocarbon, moles/liter

t = irradiation time, min.

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Manuscript received November 11, 1963; revision received June 1, 1964; paper accepted June 2, 1964. Paper presented at A.I.Ch.E. Tulsa meeting.

Optimization of Initial Composition in Adiabatic Equilibrium Gas-Phase Reactions

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Chemical reactions can usually be initiated with components in reasonably arbitrary ratios, limited to some extent by the need to utilize recycle streams, by impurities carried with the reactants, or by the availability of streams of fixed composition arising from an earlier stage in a process. Determination can be made in many cases of the composition of the initial reactant mixture which will realize the greatest equilibrium yield. De Donder and Van Lerberghe (*1*) and Prigogine and Defay (*2*) have proved formally that the components in an isothermal perfect gas reaction should be combined in the stoichiometric ratio in order to attain maximum yield. Pings (*3*) has shown that this result still holds for isothermal reactions carried out in an ideal solution but requires slight modification in dense gases where the interaction terms of the second virial coefficient are significant. In certain cases involving inerts (*4*) carried along with a given reactant, the optimum initial composition may be shifted significantly, with substantial gain in yield. Maximization of economic return (*5*) can also be used as a criterion for selecting optimum feed composition.

This paper presents the determination of the initial distribution of mole fractions required to maximize the equilibrium yield for reactions carried out adiabatically in an ideal solution. Consideration is also given to the selection of an initial composition which will result in the maximum adiabatic equilibrium temperature. In both problems, inerts are assumed absent.