The Mechanism of the Prins Reaction. VII. Kinetic Studies of the Prins Reaction of Styrenes[1]

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Pseudo-first-order rate constants of styrene disappearance for the Prins reaction and hydration of a number of *para*-substituted styrenes have been measured in water solution. By varying the concentration of formaldehyde it was found that the rate depends on the total concentration of formaldehyde hydrate and its oligomers. The Hammett ρ (using σ^+) for the Prins reaction of styrenes in water solution has been determined to be -1.61 at 75.5°.

Most of the previous studies of the acid-catalyzed condensation of formaldehyde with various styrenes have centered on the stereochemistry of the reaction.[4-7] These investigations reveal that *cis* addition accounts for a large fraction of the products, in contrast to the *trans* addition which is found to be a normal result with acyclic and aliphatic olefins.[8-12] As a result of such studies a number of possible intermediates (1-3) have been proposed for the condensation of formaldehyde with styrenes to form, ultimately, the major product of the reaction,[13,14] a 4-phenyl-1,3-dioxane.
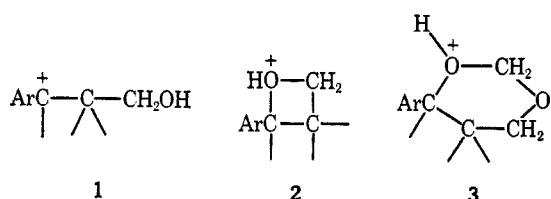
A study of the Prins reaction of styrene in acetic acid showed not only that the reaction is complex, but that, when a large excess of formaldehyde is used in 10% sulfuric acid solutions with acetic acid solvent, the major product is 4-phenyl-1,3-dioxane.[15] At low formaldehyde/styrene ratios, telomers are the major products. These results were interpreted in terms of an open carbonium-ion intermediate (1).[15] More recently, a kinetic study of the Prins reaction of α-methylstyrene in sulfuric acid solution has shown that the rate of the reaction is first order with respect to olefin and depends on the sum of the concentrations of formaldehyde hydrate and its oligomers. These results were interpreted to mean that all forms of formaldehyde in aqueous solution, hydrated monomer and oligomers,

participate equally in the reaction.[16] Smissman and coworkers have examined the kinetics of the Prins reaction of anethole in acetic acid solution as a function of the formaldehyde concentration.[17] They interpreted the results to indicate that the reaction proceeds *via* an initial fast complexation of formaldehyde and olefin followed by a slow reaction of the complex.

The present study was undertaken in an effort to provide additional evidence concerning possible alternative reaction mechanisms and the proposed intermediates (1-3). We have measured the pseudo-first-order rate constants of the Prins reaction of styrene in aqueous sulfuric acid. In addition, we have measured the Prins reaction rates and the hydration rates of a number of *para*-substituted styrenes in water solution. The rates were measured by following the styrene disappearance spectroscopically in a thermostated cell. The formaldehyde concentration was varied to determine the dependence of the reaction rate on formaldehyde species. We find that the Prins reaction of styrene in water has a first-order dependence upon the total concentration of formaldehyde species and *not* on either formaldehyde monomer or dimer concentration. We also find that reaction rates of the *para*-substituted styrenes give an excellent Hammett plot using the σ^+ values of Brown.[18]

The formaldehyde concentration dependence data are presented in Table I.

If these rates are plotted *vs.* either formaldehyde monomer concentration or *vs.* formaldehyde dimer concentration, a pronounced curvature is found at higher concentrations. This observed upward curvature, illustrated in Figures 1 and 2, shows that the rate is increasing more rapidly than expected on the basis of first-order dependence on monomer concentration or on dimer concentration. One possible interpretation of this result is that all forms of formaldehyde present are reacting with the styrene substrate. Support for this idea is found in Figure 3. This plot of the rate constant *vs.* ΣF shows an excellent linear correlation with concentration. The formaldehyde concentration, ΣF, as defined previously[19] is the sum of the molar concentrations of methylene glycol, the dominant form of monomeric formaldehyde in aqueous solutions, and all of its oligomers. Figure 4 demonstrates that the rate does not show first-order dependence upon analytical formaldehyde. The analytical formaldehyde con-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This investigation was supported in part by a Public Health Service Research Career Development Award Number 1-K3-NB-28-105 from the National Institute of Neurological Disease and Blindness.

(2) Alfred P. Sloan Research Fellow, 1965-1967.

(3) National Defense Education Act Predoctoral Fellow, 1964-1967.

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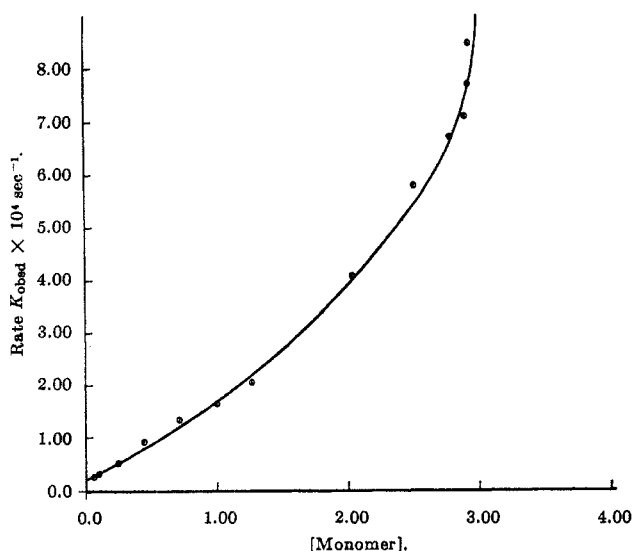
(19) See Table I, footnote *d*.

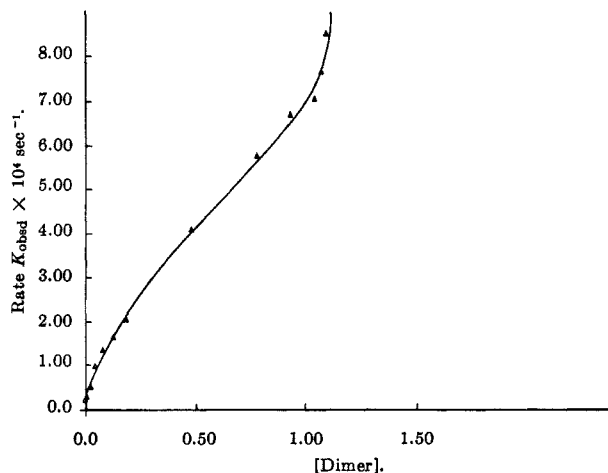Figure 1.—Rate K_{obsd} of Prins reaction *vs.* [monomer] at 60.5° in 0.97 N (average) sulfuric acid–water. Styrene is 1×10^{-4} M.

TABLE I

PRINS REACTION OF STYRENE AT 60.5° IN WATER SOLUTION[a,b]

Analytical, M	ΣF[c,d]	Mono-mer, M[e-g]	Dimer, M[e-g]	Other, M[e-h]	$K_{obsd} \times 10^4$, sec^{-1}	n[i]
0.0537	0.05	0.05	0.002	0.0000	0.266 ± 0.007	1
0.1273	0.12	0.11	0.009	0.0000	0.301 ± 0.006	1
0.2904	0.27	0.24	0.025	0.0004	0.532 ± 0.039	3
0.5366	0.48	0.44	0.047	0.0026	0.908 ± 0.407	2
0.8924	0.80	0.72	0.083	0.0094	1.347 ± 0.157	3
1.273	1.12	1.00	0.128	0.017	1.652 ± 0.062	4
1.712	1.45	1.27	0.186	0.070	2.032 ± 0.009	2
3.546	2.74	2.04	0.485	0.530	4.090 ± 0.243	4
5.360	3.75	2.51	0.780	1.29	5.781 ± 0.245	2
7.328	4.63	2.78	1.028	2.49	6.711 ± 0.273	6
8.821	5.18	2.89	1.140	3.65	7.091 ± 0.375	10
9.723	5.46	2.92	1.167	4.49	7.673 ± 0.498	10
10.72	5.73	2.93	1.195	5.40	8.521 ± 0.746	14

[a] Average sulfuric acid concentration 0.97 N. Styrene concentration 1×10^{-4} M. [b] Rate constants are not corrected for hydration which is 0.2×10^{-4} sec^{-1} at 60.5° in 0.97 N sulfuric acid. [c] Sum of the concentrations of formaldehyde hydrate and its oligomers, *i.e.*, the total concentration of formaldehyde species. [d] M. Hellin, J. Delmac, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 3355 (1967). [e] Determined by nmr methods as described by Moedritzer and Van Wazer,[f] Hellin, Delmac, and Coussement,[d] and Skell and Suhr.[g] [f] K. Moedritzer and J. R. Van Wazer, *J. Phys. Chem.*, **70**, 2025 (1966). [g] P. Skell and H. Suhr, *Ber.*, **94**, 3317 (1961). [h] Includes trimer and other oligomers as well as trioxane and is presented as analytical formaldehyde and not as the sum of the molar concentrations of the individual species. [i] Number of determinations averaged to give the reported rate constant.

centration is the total molar concentration of $-CH_2O-$ units which is determined titrimetrically.

The change of solvent from deuterium oxide to water, *i.e.*, from the analytical solutions to the kinetic solutions, might be expected to produce a solvent effect such that the equilibrium distribution of formaldehyde polymers would differ in the two systems. Such an effect has been considered and dismissed as negligible to the over-all distribution.[20] Again, a small difference in temperature (from 60.5 to 75.5°) has little effect on the polymer distribution since the formaldehyde chain–
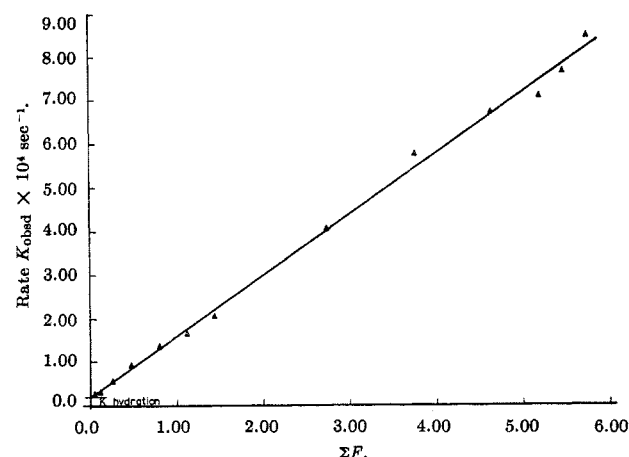
(20) See Table I, footnote *g*.

Figure 2.—Rate K_{obsd} of Prins reaction *vs.* [dimer] at 60.5° in 0.97N (average) sulfuric acid–water. Styrene is 1×10^{-4} M.

Figure 3.—Rate K_{obsd} of Prins reaction *vs.* ΣF at 60.5° in 0.97 N (average) sulfuric acid–water. Styrene is 1×10^{-4} M. Slope = 1.41 ± 0.03; intercept = 0.16 ± 0.08.

chain equilibria have a negligible temperature dependence.[21]

The rates of hydration of a number of styrenes used in the present study were determined at the same temperature and acid concentration used for the studies of the Prins reaction. These data show that the disappearance of styrene in the studies of the Prins reaction is indeed primarily due to the Prins reaction and not to the competing hydration reaction. Moreover, these data provide a ρ value for comparison with the ρ obtained for the Prins reaction of styrenes.

The study of the Prins reaction of α-methylstyrene suggests that the acidity dependences for hydration and the Prins reaction are the same. Considering this and that the highest value of the rate constant for hydration in our studies is less than one-seventh that for the Prins reaction, we can conclude that the observed rate is essentially only that of the Prins reaction. The results of the kinetic measurements for the hydration and Prins reaction of a number of styrenes are summarized in Table II.

From the Prins and hydration reaction constants in Table II it is possible to determine the Hammett ρ values for the reactions in water solution at 75.5°. The Hammett plots (using σ^+) are presented in Figure 5.
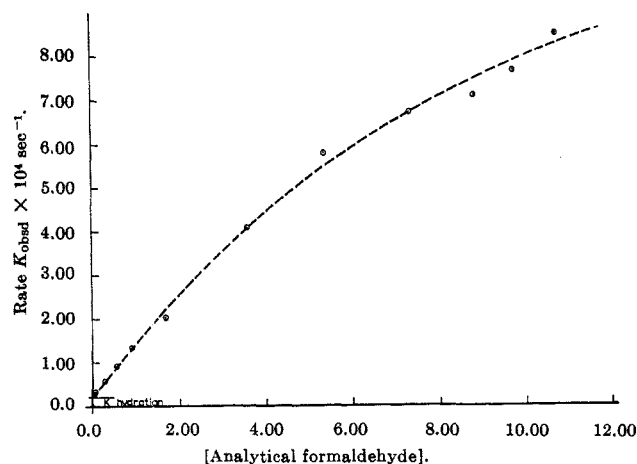
(21) See Table I, footnote *f*.

Figure 4.—Rate K_{obsd} of Prins reaction vs. [analytical formaldehyde] at 60.5° in 0.97 N (average) sulfuric acid–water. Styrene is $1 \times 10^{-4} M$.

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE HYDRATION AND PRINS REACTIONS OF STYRENES[a,b]

p-X	Solvent	Temp, °C	n^c	$K_{obsd} \times 10^4$, sec^{-1}	$K_{hydrn} \times 10^4$, sec^{-1}
H	H_2O	75.5	2	15.67 ± 0.23	
		60.5	3	4.19 ± 0.05	
		60.5	1		0.19 ± 0.003
		75.5	1		$0.78^d \pm 0.02$
Br	H_2O	75.5	2	6.99 ± 0.20	
		60.5	2	1.49 ± 0.05	
		75.5	1		$0.24^d \pm 0.01$
Cl	H_2O	75.5	3	7.41 ± 0.27	
		60.5	3	1.96 ± 0.07	
		75.5	1		$0.42^d \pm 0.02$
CH$_3$	H_2O	75.5	3	43.62 ± 4.21	
		60.5	2	13.03 ± 0.42	
		75.5	1		$5.2^d \pm 0.01$
OCH$_3$	H_2O	75.5	e	199.79	
		60.5	e	61.81	
		40.0	3	10.38 ± 0.41	
		32.7	3	5.22 ± 0.29	
		75.5	2		$28.11^d \pm 1.23$

[a] Prins reaction solvent was water containing 3.2 M formaldehyde and 0.89 N sulfuric acid. Styrene concentration 1×10^{-4} M. [b] Plotted as rate vs. σ^+ in Figure 5. [c] Number of determinations which were averaged to give reported rate constant. [d] The hydration solution was 0.96 N sulfuric acid. Infinity points were calculated using Guggenheim plots. [e] Extrapolated from measurements made at a lower temperature.

The small negative ρ of -2.1 that we observe for the hydration of styrenes requires comment. This value is substantially different from the ρ of -3.42 for the hydration of styrenes in 3.83 N perchloric acid at 25° determined by Schubert, Lamm, and Keefe in the course of their elegant studies on the hydration of styrenes.[22] As a check on our experimental methods, we repeated some of the hydration measurements in 3.83 N perchloric acid at 25°, and these results were in excellent agreement with those reported by Schubert and coworkers. Perhaps the combination of higher temperature and lower acid concentration used in the present study is enough to account for the change in ρ.

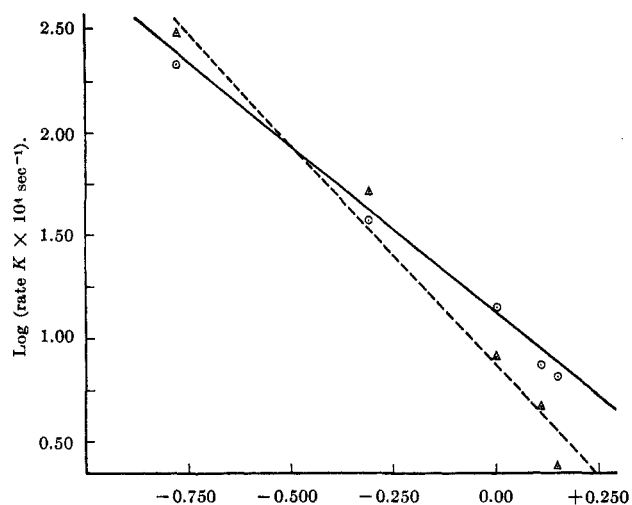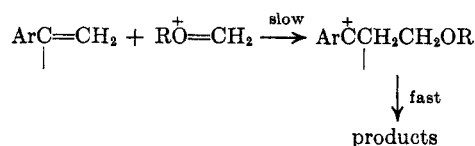Although it is difficult to compare reaction constants for reactions done under quite different conditions of

Figure 5.—Log rate K vs. σ^+ at 75.5°: – – – –, △, rate K_{hydrn}, $\rho = -2.12 \pm 0.14$; ——, ⊙, rate K_{Prins}, $\rho = -1.61 \pm 0.07$.

solvent and temperature, it is interesting to note that Okamoto and Brown[23] find $\rho = -2.34$ (using σ^+) for the stannic chloride catalyzed polymerization of styrenes in carbon tetrachloride–nitrobenzene solution (1:1).[23] Similarly, the cationic polymerization of a number of α-methylstyrenes shows $\rho = -1.7^{23}$ in carbon tetrachloride solution,[24] whereas our data indicate a maximum negative ρ of -1.61 for the Prins reaction of styrenes. Any correction for hydration would only decrease this value since the ρ for hydration is more negative than that observed for the Prins reaction. The cationic polymerization of styrenes has one major feature in common with the Prins reaction of styrenes. They both involve formation of a carbon–carbon bond as a result of electrophilic attack upon the styrene double bond.

The reaction constant for the Prins reaction of styrenes is less negative than might be anticipated for a reaction in which a full positive charge is placed on the benzylic carbon at the transition state. However, the value is not so grossly different from that observed for the hydration of styrenes under similar conditions. We conclude that the reaction constant observed for the Prins reaction of styrenes does not rule out a simple carbonium-ion mechanism and clearly does not make it necessary to propose a four-membered cyclic oxonium-ion structure for the transition state. Moreover, the lack of stereoselectivity observed for the Prins reaction of 1-phenylpropene in aqueous medium is consistent with a simple carbonium-ion mechanism.[7] The accumulated data lead us to conclude that the major pathway for the Prins reaction of styrenes in aqueous solution involves the rate-determining transfer of a positive formaldehyde species to styrene to give an intermediate carbonium ion.

$$\text{ArC}{=}\text{CH}_2 + \overset{+}{\text{RO}}{=}\text{CH}_2 \xrightarrow{\text{slow}} \text{Ar}\overset{+}{\text{C}}\text{CH}_2\text{CH}_2\text{OR}$$

$$\downarrow \text{fast}$$

$$\text{products}$$

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This mechanism is similar to that proposed for the hydration of styrenes,[22] and the same conclusion was reached by Hellin, Gaillard, and Coussemant from their study of the Prins reaction with α-methylstyrene.[16] A mechanism specifically involving a dimer of formaldehyde is not indicated by any of the data.

Experimental Section

Materials.—Chemicals were stored under refrigeration and used without further purification except where otherwise noted. p-Methyl-, p-chloro-, and p-bromostyrene were purchased from Aldrich Chemical Co. Reagent grade styrene and trioxane (>99%) were obtained from Matheson Coleman and Bell. p-Methoxystyrene was prepared from 1-(p-methoxyphenyl)-ethanol by the method of Brooks.[25]

Solvents were distilled water and 99.85 atom % deuterium oxide (Calbiochem), while the acids were reagent grade sulfuric (>98%) or 99 atom % deuterated sulfuric acid (Stohler Isotope Chemicals).

Apparatus.—The ultraviolet spectral measurements were obtained with a thermally regulated Cary 15 spectrophotometer; the temperature was read (±0.2°) at the sample cell. The sample cell consisted of the usual 10-mm quartz cuvette to which was fused a Teflon stopcock.

The nmr spectral measurements were made in sealed tubes using a Varian A-60 spectrometer in analogy with earlier work.[19-21]

Preparation of Formaldehyde Solutions.—The aqueous and deuterium oxide solutions of formaldehyde were prepared by dilution of a standard formaldehyde–sulfuric acid–water solution or a standard formaldehyde–deuteriosulfuric acid–deuterium oxide solution. These standard solutions were prepared by the depolymerization of trioxane.

All solutions were analyzed for total formaldehyde content using the iodometric method cited by Walker.[26] The acid content was determined by titration with standard base. The densities of the aqueous solutions were taken as equivalent to those presented by Natta and Baccaredda[27] while those of the deuterium

oxide solutions were obtained by extrapolation from the density measurements of Hellin, *et al.*[19]

All solutions were allowed to equilibrate at least 1 week prior to use. Solutions above 20% w/w formaldehyde were maintained above room temperature to prevent precipitation.

Kinetic Measurements.—The reactions were followed by observing the decrease in the π–π* absorption for the styrene and substituted styrene solutions. A typical run was performed as follows: To 10 ml of formaldehyde solution was added 0.1 to 0.2 μl of styrene, and the solution was agitated. Approximately 5 ml of the solution was then transferred to a 13 × 100 mm Pyrex test tube which was sealed and placed in an oil bath for later use as an infinity point sample. The uv sample cell was then filled to a mark with the remaining solution.

The Cary 15 spectrophotometer which had equilibrated for 2 hr at 60.5° ± 0.2° was adjusted using two matched water-filled 10-mm quartz cells to provide a base line of zero at 248 mμ. The instrument was set to a "sync" operation of 50 sec/div. The sample cell was preheated for 2–3 min in a 55–60° oil bath, then cleaned, and immediately transferred to the cell compartment. The disappearance of styrene was followed for at least 1 half-life. The base line was checked with the matched cells at the completion of the run to ascertain instrument stability. After at least 10 half-lives, the contents of the test tube which had been previously placed in the oil bath were cooled, transferred to the sample cell, and allowed to temperature equilibrate. The infinity value was recorded.

The rate constants were calculated using a linear least-squares fit of the integrated form of the first-order rate equation. The rate *vs.* concentration plots and the log rate *vs.* σ+ plots were similarly calculated using a linear least-squares method, assuming variance in the rate constants only. All calculations were performed with an IBM 360, Model 50, computer.

Registry No.—Styrene, 100-42-5; p-bromostyrene, 2039-82-9; p-chlorostyrene, 1073-67-2; p-methylstyrene, 622-97-9; p-methoxystyrene, 637-69-4.

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Alkanesulfonate Synthesis. I.
Ion Catalysis of Sulfite Radical-Ion Addition to Olefins

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Certain nitrate salts have unusual, significant, and practical catalytic effects on the selective addition of the sulfite radical ion in the presence of oxygen to unsaturated bonds. Specific cations and anions have selective coinitiation catalytic effects with oxygen on the conversions of olefins into alkanesulfonates. The relative reactivities of homologous 1-alkenes, mixed 1-alkenes, internal n-alkenes, branched olefins, monocyclic olefins, bicyclic olefins, dienes, and acetylenes with potassium nitrate catalysis are compared. The competition conversion of hexene isomers indicates a *cis* effect inherent in the olefin activation for addition. The mechanism of the potassium nitrate catalysis and the stereochemistry of the sulfite radical-ion addition are discussed. A mechanism involving (1) the production of sulfite radical ion, directly or indirectly, by nitrate-ion oxidation of sulfite ion, (2) bisulfite ion in the chain-transfer reaction, and (3) termination by sulfite radical-ion oxidation and radical coupling is proposed. The product mixtures containing predominantly 1-alkanesulfonates have been analyzed and characterized. The presence of nitrogen in the organic sulfonate product indicates the incorporation of nitrogen-containing radical species.

Olefin-derived 1-alkanesulfonates have excellent biodegradability and also good surfactant properties[1-4]

and hold promise of new markets for 1 olefins from cracked paraffin wax. They may directly reduce pollution problems and indirectly make more natural fats and oils available for human nutrition. These social and economic considerations, as well as organic chemical interests, make the bisulfite addition to olefins

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(3) "Alkane Sulfonate Surfactants," Technical Bulletin 2-4-0664, Esso Research and Engineering Co., Linden, N. J. (about 1964).

(4) M. C. Fuerstenau and J. D. Miller, *Trans. Mining Soc. AIME*, **153** (1967).