641. *Kinetics and Mechanism of Hydrochlorination of the Surface of Rubber Latex Particles.*

By Manfred Gordon and Thomas Carbarns.

A previously published technique for following the hydrochlorination of rubber particles in latex is applied to the particle surface locus mechanism, to which about three layers of polymer chains are accessible. The mechanism explaining the kinetics is based on a generalisation recently developed for extending the Hill–Hermans scheme of diffusion-reaction to the case of an unstable reagent. Here the double bonds of the polymer are regarded as fixed on a " liquid lattice," and a reactive species such as an ion pair [H_2Cl^+, Cl^-] diffuses in across the particle surface to react with these bonds. The reagent has a low equilibrium concentration in the aqueous phase ($\sim 10^{-13}$ mole/l.) and inside the non-polar polymer it has a short life-time ($\sim 10^{-9}$ sec.), during which it either " finds " a double bond, diffuses back into the aqueous phase, or decomposes to form inactive, covalent hydrogen chloride. This mechanism consistently interprets the effects on the rate of pressure, temterature, acidity, and particle size. A specially fine latex, of particle diameter $\sim$200 Å, was prepared in which nearly half the particle mass was accessible to the surface mechanism. The effect on the surface and bulk locus rates of admixture of sulphuric acid with the aqueous phase has been investigated.

Previous work [1] established that two reaction loci are involved in the hydrochlorination, vulcanization, and cyclization of natural and synthetic polyisoprene latices.

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[1] (*a*) Crampsey, Gordon, and Sharpe, *J. Colloid Sci.*, 1954, **8**, 185; (*b*) Gordon and Taylor, *Proc. 3rd Rubber Technol. Conference, London*, 1954, **241**.

These are the surface locus on the outside of the latex particles, and the bulk locus on the inside. In hydrochlorination, to be studied here in more detail, the two loci may react simultaneously under certain conditions, but are best isolated kinetically for separate study. At low pressure ($\leqslant 0{\cdot}33$ atm. at room temperature) the surface reaction occurs at measurable rate, while the bulk reaction is in practice immeasurably slow. At high pressures ($\geqslant 1$ atm. at room temperature), the surface reacts too quickly for accurate measurement, and its reaction locus is manifest as a positive intercept P when the much slower, linear (zero order) bulk-rate curve is extrapolated to the composition axis (Fig. 1). Thus P measures the percentage of rubber coming within the range of the surface mechanism. For particles of sufficiently large radius r (>200 Å), P is proportional to the specific surface of the particles, or inversely to r. More precisely, when a distribution of particle sizes is present, the surface-average radius $\bar{r}$ is geometrically related to P thus :

$$\bar{r} = \tau/[1 - (1 - 0{\cdot}01P)^{\frac{1}{3}}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where τ is the range or thickness of the layer accessible to the surface mechanism. This was determined [1a] to be 15 Å through electron-microscopical calibration of $\bar{r}$, and this is the value of τ used here. In vulcanization τ was <15 Å and dependent on the conditions, but in cyclization of latex τ was much larger.[1b] For the present work, a synthetic latex (Latex VI) of the finest particle size obtainable ($\bar{r} \sim 100$ Å) was used in order to raise the accuracy of kinetic analysis. As shown by the intercept P (Fig. 1, curve *d*), nearly half the polymer mass was within range of the surface reaction mechanism for this latex.

HILL–HERMANS DIFFUSION OF AN UNSTABLE REAGENT.

A molecular mechanism, which has been discussed theoretically,[2] is here to be fitted to the surface rate curves (Figs. 2—6). The starting point is the basic mechanism [3] for polymer reactions controlled by diffusion across an interface. This concerns the diffusion from an aqueous " bath " into a polymer (muscle, resin, fibre, hide, gel, etc.) of reagent molecules which are instantaneously captured at a suitable site by chemical reaction in the polymer. The site is thereby inactivated to any reagent arriving subsequently. Such a process sets up a diffusion wave travelling into the polymer, with a rather sharp boundary between the layers of polymer sites which have or have not reacted. In the reaction under discussion the reagent is some species derived from hydrochloric acid, and the polymer sites are double bonds. Contribution to the reaction rate by segmental diffusion of polymer sites, to meet the incoming reagent, has been treated by Hermans [3] but the kinetic analysis given below suggests that such co-operation from the polymer is negligible in our reaction.

The *initial* rate of surface hydrochlorination (initial slope of Figs. 2—6) is very slow compared with other Hill–Hermans reactions. This observation can be satisfactorily reconciled with the mechanism just described provided that the concentration c of the reagent species in the aqueous phase is sufficiently small. However, the high reaction order (curvature) of the rate plot is totally irreconcilable with the theory, unless some new factor is introduced (Fig. 2) to account for the rapid deceleration of the diffusion wavefront on its way into the polymer. A general kinetic treatment has been derived [2] for any law fixing the relative rate constants of successive polymer layers which duly degenerates to ordinary (non-decelerated) Hill–Hermans diffusion for the particular law appropriate to it. The new factor causing the deceleration in surface hydrochlorination is taken to be the *instability* of the diffusing reagent. A parameter is introduced in the form of the stability constant s, which measures the fixed probability of a reagent molecule's surviving a diffusion jump from one polymer layer to the next without decomposition. It appears sound to expect that reagents originating in a highly polar aqueous medium and diffusing into a non-polar polymer should be susceptible to deactivation, decomposition, and neutralization. The rate curves can be well fitted (Fig. 2) on this basis, though, naturally, s has to be adjusted. The variable range of the surface locus

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[2] Gordon, *Proc. Roy. Soc.*, 1955, *A*, **228**, 397.

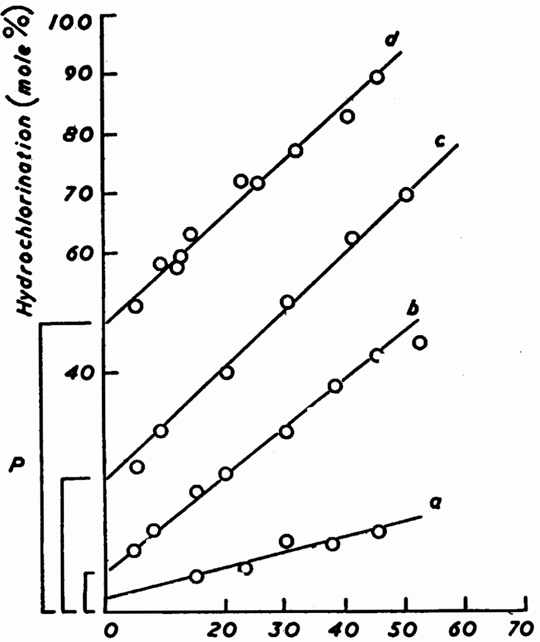
[3] Cf. Hill, *ibid.*, 1928, *B*, **104**, 39; Hermans, *J. Colloid Sci.*, 1947, **2**, 387.

reactions is accommodated by the theory, in that s should vary from one reagent to another. In Fig. 2 the theoretical curves are seen to level off sharply after the equivalent of between one and four layers has reacted, according to the value chosen for the stability constant in the range $0 \leqslant s \leqslant 0{\cdot}6$.

We now summarize the essential mathematical theory of the kinetics of an unstable reagent in a Hill–Hermans reaction. For a plane interface, or spherical particles of $\bar{r}$ exceeding about 200 Å, the rate law becomes:

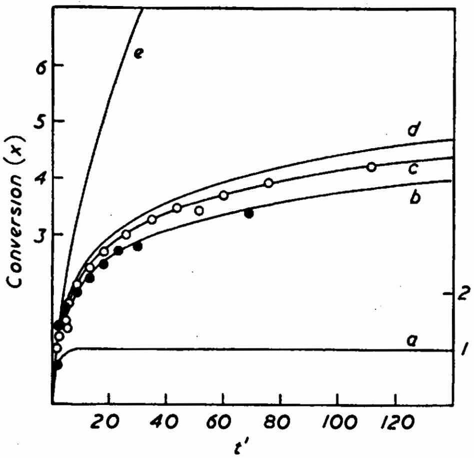
$$H = \sum_{i=1}^{\infty}\left(\sum_{a=1}^{\infty} C_{a,i,s}\right)[1 - \exp(-k_{i,s}\,t')] \quad . \;. \;. \;. \;. \;. \quad (2)$$

FIG. 1. *Bulk locus rate curves* (300° K, 2 *atm.* HCl) *as a function of particle size.*



(*a*) Natural *Hevea* latex (surface average particle diameter ~4500 Å), (*b*) synthetic latex I (1175 Å), (*c*) synthetic latex II (467 Å), (*d*) synthetic latex VI (~180 Å). The intercepts P are a measure of the specific surface available to the immeasurably fast surface locus.

FIG. 2. *Theoretical surface locus rate curves* (*eqn.* 2) *for various reagent stabilities s.*



(*a*) A completely unstable reagent ($s = 0$) leads to a first-order reaction of the outermost layer only. (*b*) $s = 0{\cdot}6$. (*c*) $s = 0{\cdot}548$; ○ synthetic latex V, 69·9°, 167 mm. partial pressure of HCl. (*d*) $s = 0{\cdot}465$; ● synthetic latex V, 26·7°, 163 mm. partial pressure of HCl. (*e*) Hill–Hermans reaction of a completely stable reagent ($s = 1$).

The amount of reaction, measured in multiples of the complete reaction of the surface layer of polymer, is denoted by H. The constants $C_{a,i,s}$ are

$$C_{a,i,s} = \prod_{j=1}^{a} k_{j,s}/(k_{j,s} - k_{i,s}) \quad (i \neq j) \quad . \;. \;. \;. \;. \;. \;. \quad (3)$$

$$C_{1,1,s} = 1$$

The rate constant $k_{i,s}$ refers to the i-th layer of polymer molecules from the interface; for the special case of instability of the reagent $k_{i,s}$ is given thus as a function of s:

$$k_{i,s} = \sinh(\operatorname{sech}^{-1} s)/\sinh(i \operatorname{sech}^{-1} s) \quad . \;. \;. \;. \;. \;. \quad (4)$$

The dimensionless " time " unit t' is related to the time t in seconds through the unknown

FIGS. 3 and 4. *Invariance of the shape of the surface rate curves under a change in* HCl *pressure.*

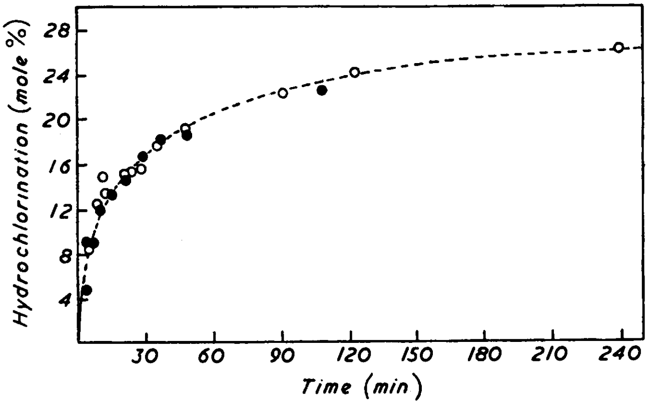


FIG. 3.

Synthetic latex V, 300° K, ○ 249 mm. partial pressure of HCl; ● 163 mm. (measured times multiplied by 0·448).

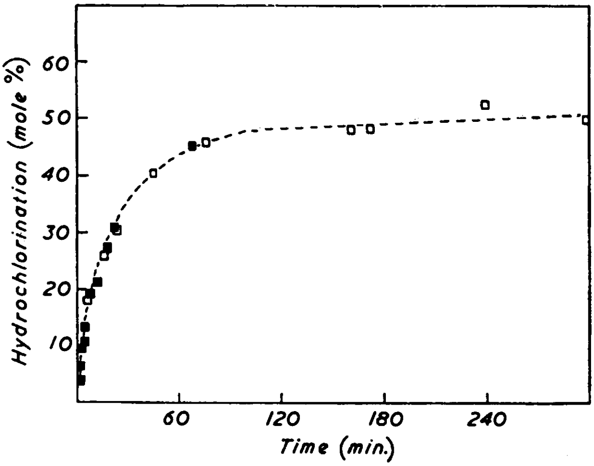


FIG. 4

Synthetic latex VI, 300° K, □ 249 mm. partial pressure of HCl; ■ 57 mm. (measured times multiplied by 0·1105).

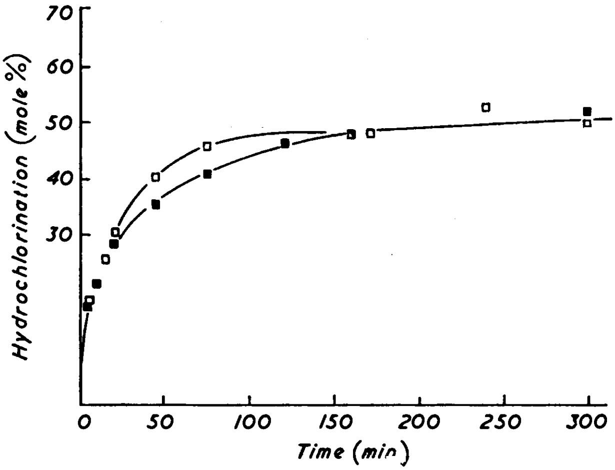


FIG. 5. *Effect of sulphuric acid on the surface locus hydrochlorination rate.*

□ Synthetic latex VI, 249 mm. partial pressure of HCl; ■ the same in presence of 17% H_2SO_4.

gross inward flux ϕ in moles of reagent per sec. per cm.^{2} of surface, and to the number m_1 ($\sim 6 \times 10^{-6}$) of moles of unsaturation in one cm.^{2} of rubber surface :

$$t' = t\,\phi\,/m_1 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Because the flux is unknown, the scaling of the time axis of our experimental plots is subject to an adjustable factor (ϕ/m_1). The flux ϕ is proportional to the concentration c of the reagent and its diffusion constant D, both measured in the aqueous phase, according to Collins's equation

$$\phi = Dc\,\alpha/l \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Here l is the length of a diffusion jump in that phase (say 1 Å), and the "accommodation coefficient" α may be taken as unity, *i.e.*, by assuming perfect absorption at the particle surface without reflection of reagent species back into the water. The spacing between rubber chains is 5 Å. The relation allowing the reaction progress H to be computed from the measured fractional conversion C is therefore, by simple geometry :

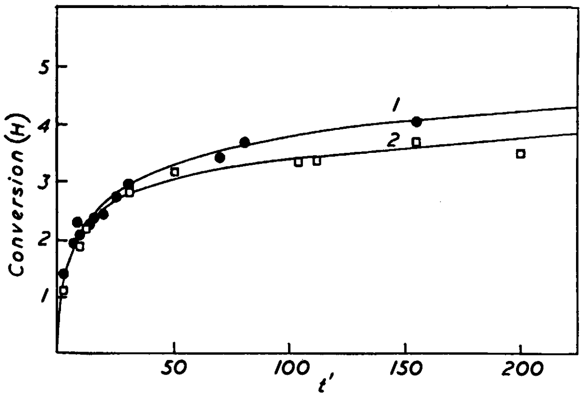


FIG. 6. *Effect of particle curvature on surface locus rate curve.*

● Synthetic latex V, 300° K, 249 mm. partial pressure HCl; particle radius $r > 200$ Å; curve 1 is drawn for $s = 0{\cdot}465$, eqn. 2 or 12 being used ($L > 40$).
□ Synthetic latex VI, 300° K, 249 mm. partial pressure HCl; particle radius ~ 90 Å; the curve 2 is drawn for $s = 0{\cdot}465$, eqn. 12 ($L = 18$).

$$H = C\bar{r}/15 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

For particles of $L < 40$ layers (*i.e.*, $\bar{r} < 200$ Å) where L is the number of layers, curvature of the interface progressively changes the rate curve. It may be shown that, as a first approximation, eqn. (2) may be amended to allow for curvature, thus

$$H = \sum_{i=1}^{\infty}\left[\sum_{a=1}^{\infty} C_{a,i,s}\,(L - a + l)^2/L^2\right]\left\{1 - \exp[-k_{i,s}\,t'L^2/(L - i + l)]\right\} \ . \qquad (8)$$

The average number of diffusion jumps executed by the reagent in the polymer before deactivation (in the absence of double bonds) is

$$\bar{N} = 1/(1 - s) \ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

The jump length between adjacent rubber chains being 5 Å, the average lifetime of the reagent while performing $\bar{N}$ jumps is given by the Einstein law

$$\bar{t} = (5\bar{N})^2/2D_{\mathrm{R}} \ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

where D_{R} is the diffusion coefficient of the reagent through the polymer. Since

$$1/(1 - s) = \bar{N} \propto \text{rate of diffusion/rate of deactivation} \ . \quad . \quad . \qquad (11)$$

it follows that the difference $\delta(\Delta E)$ between the activation energies for diffusion and for the deactivation reaction is reflected in the change of s with temperature, thus

$$\delta(\Delta E) = -2{\cdot}3\boldsymbol{R}\,\delta\log[1/(1 - s)]/\delta(1/T) \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The model on which the kinetic theory had been derived implies that the rate-controlling transition state of the surface reaction is the passage of the reagent species from the water phase to the polymer through the interface. This follows because the rate of surface reaction is proportional to the flux ϕ (eqn. 5) of reagent across the interface, while a reagent species once arrived within the polymer reacts without further energy requirement, every collision with a double bond being assumed to result in reaction.

Application of the Theory to the Hydrochlorination of Rubber.—In the *bulk* locus hydrochlorination reaction, the rate-controlling step, which must take place inside the rubber phase, was previously suggested[4] to be :

$$2HCl \longrightarrow [H_2Cl^+, Cl^-] \qquad (13)$$

The reagent in the *surface* reaction is taken to be an ion pair $[H_2Cl^+, Cl^-]$, which exists in low equilibrium concentration c in the aqueous phase. When the ion pair penetrates into the rubber, it is "snapped up" by a double bond to form a rubber hydrochloride unit, and to liberate the proton-solvating molecule of HCl in inactive, covalent form. However, if the reagent ion pair fails to meet a double bond, it will be rapidly deactivated by the reverse reaction to its formation : this reversion is expected to require little activation energy. It is this rapid deactivation to form two molecules of covalent hydrogen chloride which restricts the range of the surface reaction.

Throughout our theoretical interpretation, the adsorbed layer of non-ionic stabiliser (Vulcastab LW) has been ignored, because variations in the nature and concentration of the stabilizer leave the kinetics of latex reactions unaffected.[5] Because two adjustable parameters are involved in the fitting of experimental curves (Figs. 2—6), *viz.*, s and the scaling factor ϕ/m_1, the fit obtained, though excellent, cannot be taken to establish the mechanism on which the curves are derived. However, the effects studied in the next section support the underlying ideas.

DISCUSSION OF EXPERIMENTAL RESULTS

Effect of Pressure.—An increase in the pressure of hydrogen chloride is reflected in an increase in the equilibrium concentration c of the reagent species (ion pair) in the aqueous phase. This results in a proportionate rise in ϕ (eqn. 6), and hence in t' (eqn. 5). Experimental confirmation of this prediction is presented in Figs. 3 and 4 for two latices of different particle sizes and for pairs of pressure values. In each case, the experimental curve at the lower pressure has been adjusted (Table) by multiplication with a suitable factor of all the experimental time values, whereby the curve is brought into coincidence with that obtained at the higher pressure. The scaling factor is equal to the ratio of the two flux rates. This finding provides confirmation of the irrelevance of diffusion of rubber segments to the interface. Since the flux of the reagent species alone controls the shape of the rate curve, the assumption of *stationary* rubber sites (double bonds) in the basic model is vindicated. The adequacy of the assumption is at first sight surprising. Some mixing with the original polymer by segmental diffusion of rubber hydrochloride units which have reacted might be expected to occur during the periods of minutes or hours involved in the rate curves. The success of the theory of stationary polymer sites is probably due to the immiscibility of rubber hydrochloride with rubber chains which have not reacted. Independent observations confirm the incompatibility of the two pure polymers at the reaction temperature.

Apparent flux rates of reagent from the time scales of Figs. 3 *and* 4.

Figure	3	4	3	4	6
Latex	V	VI	V	VI	V
Total pressure (H_2O + HCl) (mm. Hg)	255	255	170	65	255
Partial pressure of HCl (mm. Hg)	249	249	163	57	167
Temperature	26·7°	26·7°	26·7°	26·7°	69·9°
Flux (ϕ/m_1) (min.$^{-1}$)	0·67	0·67	0·30	0·074	0·30

Both the isolated bulk and surface hydrochlorination rates vary approximately as powers of the partial pressure p of hydrogen chloride. The bulk rate varies as $p^{3·9}$

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[4] Crampsey, Gordon, and Taylor, *J.*, 1953, 3925.

[5] Cf. Gordon, *Ind. Eng. Chem.*, 1951, **43**, 386.

according to the slope of the logarithmic plot (II, Fig. 7) over the range 760—1900 mm. This plot refers to measurements on natural (*Hevea*) latex, but syntheric polyisoprene gives results in close agreement.[1b,4] The surface hydrochlorination rate, according to plot II (Fig. 7), varies only as $p^{1\cdot6}$ or thereabouts. A dependence of the rate on p^2 would be predicted if the diffusion flux ϕ of the reactive ion pair [H_2Cl^+, Cl^-] is assumed to be strictly proportional to its thermodynamic activity. As this assumption is, at best, approximate, the small discrepancy is of no consequence.

Mean Life-time and Concentration of the Transient Reagent Species.—The experimental curves (Fig. 2) require values of $s \sim 0\cdot5$ to fit the kinetic theory. Equation 9 shows that the reagent species is deactivated on the average after two diffusion jumps in the polymer, *i.e.*, after describing a diffusion path of 10 Å. The diffusion coefficient D_R of the ion-pair reagent is estimated to be $1\cdot5 \times 10^{-6}$ cm.^{2}/sec. from Grün's measurements[6] on substances of various molecular weights diffusing through rubber. Equation 10 then leads to an average mean life-time of the ion-pair reagent of only 3×10^{-9} seconds. The experimental values of ϕ/m_1 (Table), taken with eqn. 6, lead to estimates of 6×10^{-13} to 6×10^{-12} moles/l. for the concentration of the reagent ion pair in the aqueous phase between 50 and 250 mm. Hg of hydrogen chloride. (For this calculation, the diffusion coefficient D of the reagent through the aqueous phase is taken as that valid for hydrogen chloride itself, *i.e.*, $2\cdot5 \times 10^{-5}$ cm.^{2}/sec.) For comparison with the estimates of the ion-pair concentration, we quote estimates ranging from $5\cdot9 \times 10^{-12}$ to 4×10^{-8} moles/l. for undissociated hydrochloric acid, as distinct from ion pairs, in 0·01—1·0N-HCl.[7] The calculations of this section illustrate the fact that surface hydrochlorination depends on the thermal bombardment of the rubber surface by a short-lived and dilute reagent.

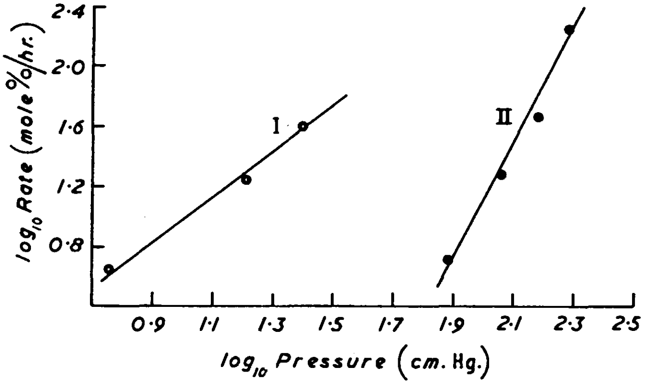

FIG. 7. *Pressure dependence of surface and bulk locus rates.*

(I) Initial surface locus rate (100 ϕ/m_1 hr.$^{-1}$). (II) Unretarded zero-th order bulk locus rate.

Effect of Admixture of Sulphuric Acid.—Reductions of the overall concentration of hydrogen chloride in water can be made, at constant hydrogen chloride pressure, by admixture of sulphuric acid, an acid somewhat stronger than hydrochloric acid at equal concentration. At high concentration of sulphuric acid, incursion of the acid-catalyzed cyclization of rubber as a side reaction is to be feared, whose rate (in the absence of hydrogen chloride) becomes measurable above about 60% of H_2SO_4 in the aqueous phase.[8] We have, therefore, compromised by studying the effect on the kinetics of hydrochlorination of an aqueous phase composed of 17 : 83 H_2SO_4–H_2O (w/w). As shown in Fig. 5, this appreciable change in the acidity of the original aqueous medium produces very little change on the surface hydrochlorination rate. The initial rate is unchanged within the small experimental error. Indeed, the only alteration in the rate curve due to the addition of sulphuric acid is a moderate variation which appears in the middle range and remains unexplained.

The activity of water must be expected to vary considerably when 17% of sulphuric acid is added. The invariance of the hydrochlorination rate shows that the equilibrium

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[6] Grün, *Experientia*, 1947, **3**, 491.

[7] Wolfenden, *Ann. Reports*, 1932, **29**, 21.

[8] Gordon, *Proc. Roy. Soc.*, 1951, *A*, **204**, 569.

concentration *c* of the reagent species depends only on the activity (vapour pressure) of hydrogen chloride, and not on the activity of water. This confirms that the reagent is formed from an integral number *n* of HCl units, and thus carries no net ionic charge, in conformity with eqn. 13.

Effect of Temperature.—At constant pressure, the *bulk* locus hydrochlorination reaction has an apparent negative activation energy[4] of −6 kcal./mole. In contrast, the *surface* hydrochlorination rate dH/dt' is found to be virtually independent of temperature, as well as of added sulphuric acid. The initial rate does not vary measurably at three temperatures over the 42° range studied (a curve at 44° has been omitted from Fig. 2). The estimated accuracy of these measurements leads to the limits $E = 0 \pm 1{\cdot}5$ kcal./mole for the activation energy. This means that the energy state of the reagent, when passing through the rubber surface, is practically on a level with the corresponding number of covalent molecules of hydrogen chloride in the gas phase. Thus, when passing into the rubber, the reagent must be largely stripped of its hydration shell, which supports the conclusion that it does not contain water. The shape of the rate curve does change slightly, but definitely, with temperature, in a way accommodated by the theory. Plots *b* and *c* in Fig. 2 interpret the change in shape between 26·7° and 69·9° as a change of the order of 20% in the stability constant *s*. According to eqn. 12, this corresponds to a value of $\delta(\Delta E) \sim 1$ kcal. Such a small difference between the energies of diffusion and of the deactivation process reflects the fact that both these energies should, in theory, be individually small.

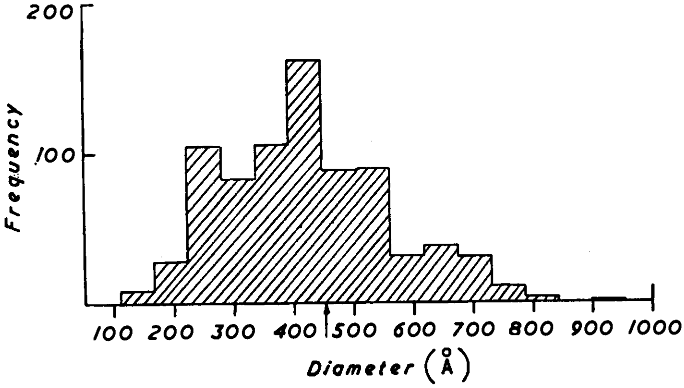

FIG. 8. *Apparent size distribution curve of the* 791 *particles on a micrograph of synthetic latex* VI, *shadow cast with* Au/Pd *alloy. The calculated apparent surface average diameter is marked by an arrow.*

Effect of Curvature.—Even for the smallest particles available (Latex VI), the expected effect of curvature on the surface hydrochlorination kinetics is not yet very appreciable. Fig. 6 suggests that the observed deviations of the rate curve of Latex VI are in the expected sense and of the right order of magnitude. To show this, we have drawn plot 2 as the theoretical curve of eqn. 8 with $L = 18$ (*i.e.*, $\bar{r} = 90$). The actual radius $\bar{r}$ of Latex VI is 76—110 Å. The heterodisperse nature of the latex (Fig. 8) would have to be taken into account if the theory were to be refined beyond the first approximation inherent in eqn. 8. The accuracy of the present results does not warrant such refinements.

Effect of Sulphuric Acid on the Bulk Rate.—It was found (Fig. 5) that the presence of 17% of sulphuric acid in 83% of water affected the surface locus rate curves negligibly. The presence of a similar percentage (20%) of sulphuric acid exerts only a small deceleration of the bulk locus reaction measured at 2 atm. of HCl. However, as shown in Fig. 9, this effect takes an interesting form when natural (*Hevea*) latex is used, which confirms the interpretation given[9] of the early linear slow portion of the rate curve, which is observed only with natural latex. It was suggested that this latex contains a retarder which deactivates a fixed number of the ion-pair reagents in the bulk locus reaction, before the full linear rate curve takes over at the " kink." The figure shows that slope of the retarded portion preceding the kink is not measurably affected by sulphuric acid, while the subsequent, unretarded, portion is definitely reduced in slope (rate). In accordance

[9] Gordon and Taylor, *J. Appl. Chem.*, 1955, **5**, 62.

with the theory of retardation given by Gordon and Taylor,[9] the two unretarded rate lines extrapolate back to the point −27% on the conversion axis, as did six curves obtained by these authors under a wide variety of HCl pressures and temperatures. The constant negative intercept of the unretarded rate line is interpreted as the integrated total of the retardation effect, just as the positive intercept of the retarded rate plot (preceding the kink) is interpreted as the measure of the fast surface reaction.

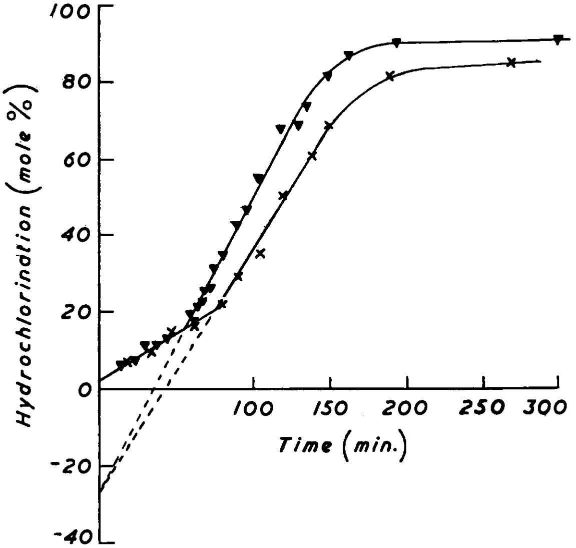

FIG. 9. *Effect of sulphuric acid on the bulk locus rate of hydrochlorination at* 300° K *and* 2 *atm. of* HCl.

▲ In absence of H_2SO_4; × in presence of 20% H_2SO_4.

EXPERIMENTAL

Full details have been published of the general method of preparing the latices, of the micro-reaction vessel used for their hydrochlorination, and of the density gradient technique for following this reaction in terms of the density of the purified polymer.[1b,4,9] In order to prepare a latex of the smallest attainable particle size (Latex VI) a higher temperature, greater dilution of the monomeric isoprene, high ratio of stabilizer (Vulcastab LW) to isoprene, and shorter polymerisation time than usual were employed. These factors favour the production of finer particles in emulsion polymerization.[10] The detailed formulation of Latices V and VI were respectively: isoprene 10 g., 1·4 g.; water 15 g., 20 g.; 20% Vulcastab LW in water 4 g., 4 g.; ammonium persulphate 0·25 g., 0·05 g. The reagents were sealed in glass ampoules under carbon dioxide and shaken at 49° for 9·5 hr. (Latex V) and 60° for 2 hr. (Latex VI).

The usual size determination from the intercept P and eqn. (1) gave a value of $\bar{r}$ = 230 Å for Latex V. For Latex VI this method leads to $\bar{r}$ = 76 Å. Attempts to verify this value by direct electron microscopical determination encountered some difficulty. The small particles were insufficiently well resolved for size measurement without metal shadowing. Shadowing did give excellent resolution, but the results so obtained are known to be too high. The correction applicable for larger particles [1a] consists in subtracting 115 Å from the measured radius, in agreement with findings by Kern and Kern [11] for polystyrene latex. Statistical evaluation of the 791 particles visible on a shadowed micrograph gave a distribution curve (Fig. 8) much less sharp than those of the coarser Latices I—V, with an uncorrected value of $\bar{r}$ = 226 Å. Application of the correction mentioned leads to $\bar{r}$ = 111 Å. While this agrees reasonably with the value of 76 Å from the intercept P and with the kinetic effect due to curvature (Fig. 6), the correction here exceeds the radius of the smallest shadowed particles visible, which throws some doubt on its validity in the range of very small particles.

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[10] Harkins, *J. Amer. Chem. Soc.*, 1947, **69**, 1428.
[11] Kern and Kern, *J. Appl. Phys.*, 1950, **21**, 705.