803. *Kinetics and Mechanism of Hydrochlorination of Synthetic and Natural Polyisoprene Latex.*

By Edward Crampsey, Manfred Gordon, and James S. Taylor.

The kinetics of hydrochlorination of synthetic polyisoprene emulsions, prepared by new and simple methods, are studied for comparison with the same reaction of natural latex. Nearly identical zero-order rate constants apply to both substrates at 300° K and 1 or 2 atm. of hydrogen chloride, despite differences in the detailed structure of the polymers. The conclusion that the substrates are not concerned in the rate control follows, since the rates of chain reactions which might give zero-order constants are very sensitive to the detailed structure of the polymers. Two initial rate abnormalities are observed. The first is shown to be due to a fast surface reaction, and the second probably reflects the presence of a basic retarder in natural rubber particles only. Similar abnormalities of the cyclization reaction, reported earlier, are explained similarly.

The effects of energetic factors and concentration on the hydrochlorination rate support visualization of the simple rate-determining step as: $H^+ + Cl^- \longrightarrow (H^+, Cl^-)$ (ion pair), where the proton is probably solvated as H_2Cl^+. The critical transition state must be uncharged, as the reaction rate is unaffected by a change in dielectric constant due to the conversion of rubber hydrocarbon into rubber hydrochloride. Existence of the ion pair as reactive intermediate confirms Gordon and Taylor's recent stereochemical theories on hydrochlorination of natural rubber. The rapid surface reaction is ascribed to the ready formation of ion pairs or similar species in the aqueous phase, and the limited range (about 15 Å) of the surface reaction to the slow rate of diffusion of unchanged rubber units to the surface.

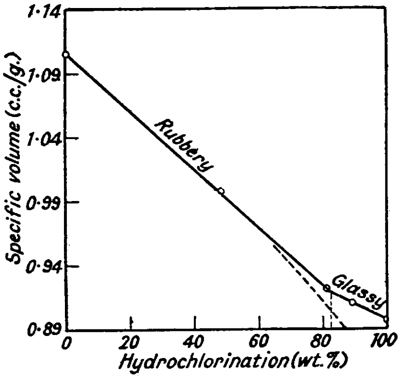
As an aid to the elucidation of the mechanism of the hydrochlorination of Hevea rubber latex (van Veersen, Proc. 2nd Rubber Technol. Conf., 1948, p. 87) (for introductory paper see Gordon and Taylor, *J. Appl. Chem.*, in the press), synthetic polyisoprene latices have been prepared and studied kinetically. The prime motive for this work was the desire to ascertain the effect on the hydrochlorination rate of a change in the chemical nature of the substrate. The variation of particle size in the synthetic latices, and the absence of the varied contaminants from which the natural latex cannot readily be freed, have led to effects which shed new light on the reaction.

Apart from the non-rubber constituents present in natural latex, a stabilizer has to be added against acid coagulation. To this end we have used Vulcastab LW, a non-ionic ethylene oxide condensation product (marketed by Imperial Chemical Industries Limited), of whose concentration the hydrochlorination rate of natural latex has been shown to be independent (*idem, loc. cit.*). Simple emulsion-polymerization methods were, therefore, tried with this substance as the surface-active ingredient in the hope of preparing synthetic polyisoprene latex stable to subsequent acidification and reaction with hydrogen chloride. In view of the complexity of emulsion-polymerization methods recorded for isoprene (*e.g.*, U.S.P. 1,896,491), it was with surprise that we found that suitable latices can be smoothly prepared without ingredients other than isoprene monomer, water, Vulcastab LW, and ammonium persulphate (catalyst). It is true that as much as 8% of Vulcastab LW, calculated on the isoprene, was found desirable and that some little coagulum formed even with this amount. However, the coagulum could readily be filtered off, and the latex was then of fine and uniform particle size. The latex was completely stable to acid and could not be flocculated by the usual technique of dilution with boiling water. Acetone was therefore used to coagulate the partially hydrochlorinated polymer at the end of each kinetic experiment.

Experimental

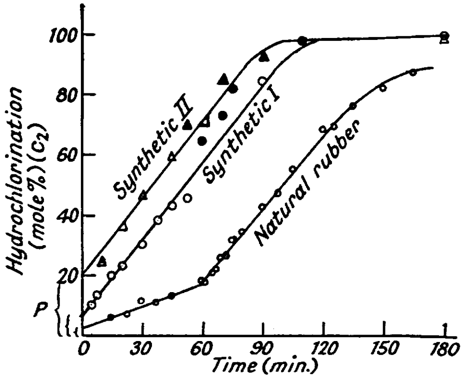
Two latices (I and II) were used for hydrochlorination studies. They had the respective compositions: isoprene 3·5, 4·0; water 1·5, 5·0; 20% Vulcastab LW in water 1·5, 1·5; and ammonium persulphate 0·075, 0·085 g. They were sealed in soft-glass ampoules and shaken for 19 hr. at 60° (latex I) and 4½ hr. at 57° (latex II). The isoprene was from British Drug Houses Ltd., and the fraction, b. p. 34·5—35·5°, served for latex I. For latex II a broader fraction (34·5—37°) was taken. The accepted b. p. is 34·1°. Further purification of the isoprene was not deemed necessary, as the rate of the hydrochlorination was found to be practically independent of the nature of the rubber hydrocarbon (see below). The monomer remaining after polymerization was removed by blowing carbon dioxide over the warmed latex under a partial vacuum. The main difference between the two latices was a three-fold reduction of particle size in latex II, attributed to the higher dilution with water and shorter polymerization. Each latex was diluted with a little water and then two-fold with concentrated hydrochloric acid, filtered through glass cloth, and stored in a corked bottle.

FIG. 1. *Specific volume as function of composition of polymer.*



——— *Synthetic latex I.*
– – – – *Natural latex.*

FIG. 2. *Hydrochlorination kinetics of polyisoprenes at* 300° K *and* 2 *atm. of* HCl.



Full circles and full triangles : after prolonged storage.

FIG. 3. *Hydrochlorination kinetics of synthetic latex II at* 300° K *and* 1 *atm. of* HCl.

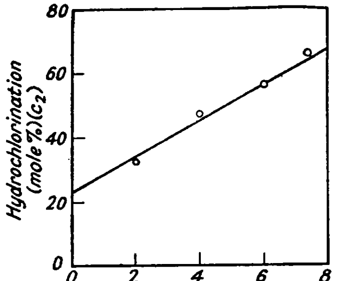
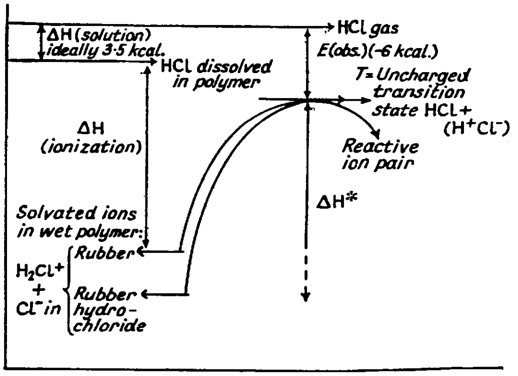


FIG. 4. *Possible energy levels of precursors in hydrochlorination.*



The apparatus and procedure for hydrochlorination kinetics were those described by Gordon and Taylor (*loc. cit.*). Fig. 1 shows the calibration curve for the specific volume of the purified polymer against wt. % conversion, compared with a similar plot for natural rubber (see Discussion). By its means the wt. % (and hence the mole %) hydrochlorination was found for the polymer of each kinetic experiment from its density, measured in a diffusion gradient tube. Figs. 2 and 3 present the results of the kinetic experiments at 300° K and at 2 and 1 atm. respectively of HCl pressure.

When the synthetic polyisoprene latices were acidified with an equal volume of concentrated hydrochloric acid, they became, unlike natural latex, of limited chemical stability. When it was noted that points taken (full circles and full triangles) after a few weeks' storage gave results markedly different from those obtained in the earlier kinetic experiments, the density of the supposedly unchanged polymer in latex I was redetermined. It showed an increase from 0·904$_7$ to 0·924$_2$. This could be attributed to 7 mole % hydrochlorination, and a small amount of chlorine was found in the purified polymer. The kinetic evidence on this stored latex, however, suggests that some change other than hydrochlorination had also occurred. This is likely to be oxidation, against which Hevea latex is effectively protected by natural antioxidants, but to which the synthetic latex might well be sensitive. The lines drawn through the points in Figs. 2 and 3 have the slopes and intercepts recorded in the Table. It will be noted that the slopes are all about 8% higher than those for natural rubber under the same conditions. This difference, though outside the experimental error, is almost negligible and is probably due to effects of the medium on the rate.

DISCUSSION

The density and kinetic measurements of the hydrochlorination of synthetic polyisoprene show interesting parallels with, and differences from, those of natural rubber latex.

	Intercept *P* in Fig. 2 (mole %)	Slope of " retarded " line (mole %/hr.)	Slope of main line (mole %/hr.)	Intercept *P* in Fig. 2 (mole %)	Slope of " retarded " line (mole %/hr.)	Slope of main line (mole %/hr.)
	Fig. 2 (2 *atm. of* HCl).			*Fig.* 3 (1 *atm. of* HCl).		
Natural (Hevea) latex	2·0	14	47·5	2·5	1·5	5·2
Synthetic latex I	6·25	None	51	—	—	—
Synthetic latex II ...	20·0	None	51	23	None	5·6

Density Measurements.—Samples of latex I polymer gave the plot of specific volume *V* against composition shown in Fig. 1. This is of the type explained by the " ideal copolymer " theory (*idem, ibid.*, 1952, **2**, 493) and is very similar to the analogous plot for butadiene–styrene copolymers, if styrene is imagined to take the place of a hydrochlorinated unit. Preliminary measurements in this laboratory confirm that the kink in the plot (Fig. 1), around 80 wt. % hydrochlorination, is associated with the composition having its second-order transition at the temperature (300° K) concerned. The equation for the " rubbery " line of the plot is :

$$V = 1{\cdot}106 - 0{\cdot}00226c_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where c_2 is the wt. % of hydrochlorinated units. For natural rubber and its hydrochloride, the " rubbery " line is almost identical ($V = 1{\cdot}106 - 0{\cdot}00230c_2$), but deviates markedly downwards at high c_2. The deviation is due to the crystallinity (van Veersen, *loc. cit.*) of the hydrochloride of natural rubber. Synthetic polyisoprene hydrochloride has previously been found to be amorphous (D'Ianni, Naples, Marsh, and Zarney, *Ind. Eng. Chem.*, 1946, **38**, 1178), and this was confirmed by us by electron diffraction as well as by the " ideal " shape of the plot in Fig. 1. The packing aspects of this plot will be discussed elsewhere. Latex II gave a starting polymer ($c_2 = 0$) of slightly lower specific volume, *viz.*, 1·098 instead of 1·106. Equation (1) was adjusted accordingly when computing c_2 from the density, and a similar parallel displacement made for the " glassy " line. The effect is likely to reflect the inclusion of small amounts of a higher-boiling fraction (see p. 3926) as a contaminant of the isoprene.

Kinetic Measurements.—In the light of the following facts synthetic polyisoprene is to be regarded as a different substrate from natural rubber in the hydrochlorination reaction. D'Ianni (*Ind. Eng. Chem.* 1948, **40**, 253) found that only 88—90% of the units were polymerized by 1 : 4-addition in isoprene emulsion polymer, so that 10—12% were probably in the 1 : 2- or 3 : 4-forms scattered along the polymer chain. Richardson and Sacher (*J. Polymer Sci.*, 1953, **10**, 353) confirmed this by infra-red analysis, since for a typical persulphate-catalysed emulsion polyisoprene they found 5% of 1 : 2- and 5% of 3 : 4-units. Moreover, 72% of the units were in the *trans*-state and only the remaining 18% were *cis*-isoprene units as found in natural rubber. *trans*-Units also predominate over *cis* in synthetic polybutadiene (Hart and Meyer, *J. Amer. Chem. Soc.*, 1949, **71**, 1980). Synthetic polyisoprene thus differs from rubber as a substrate in that it does not consist predominantly of long sequence of *cis*-units in 1 : 4-addition. The irregularity of the structure of polyisoprene is reflected in the non-crystalline nature of its hydrochloride mentioned above. A comparative discussion of the hydrochlorination kinetics of the two substrates centres on the initial " jump " in the rate curves, the retardation effect, the main straight-line portion of the rate curves, and the total conversion which is asymptotically reached.

Extrapolation of the relevant straight-line portions to the composition axis reveals (Fig. 2) that different percentages (P) of the total polymer are involved in the " initial jump " under comparable conditions (2 atm.), *viz.*, 2% of the natural rubber, 6·25% of latex I, and 20% of latex II units. In principle this fast reaction could be due to the presence of corresponding percentages of units either with a chemically more reactive structure, or lying at a site favoured for reaction. Correlation of P with the surface-average particle size, measured by the electron-microscope, proves that the fast units lie within 15 Å of the particle surface. This proof that the initial jump is a surface reaction, which implies that the subsequent main part of the hydrochlorination occurs in the bulk of the polymer particles, will be published in detail elsewhere.

The " retardation " effect in natural rubber latex, which leads to a slow linear rate before the full rate is suddenly attained (Fig. 2), is entirely missing in synthetic polyisoprene. This confirms that the effect is not an essential part of the hydrochlorination mechanism, and lends much support to the suggestion already made tentatively (Gordon and Taylor, *loc. cit.*) that a special retarding substance is present inside the natural latex particle. Indeed, the surface reaction and the retardation effect in natural latex hydrochlorination exposed in this paper explain satisfactorily observations on the cyclization kinetics of the same substrate, in which an initial " jump " followed by a retarded rate were also found (Gordon, *Proc. Roy. Soc.*, 1951, *A*, **204**, 570) : these initial-rate abnormalities were not then explained, apart from a reference to possible diffusion effects. The two reactions are thought to go through a common intermediate (Gordon and Taylor, *loc. cit.*) and their rates are both very sensitive to acid concentration. This suggests the presence of some basic substance in Hevea latex particles, which until it is neutralized or destroyed, diminishes both rates by diminishing the prevailing acidity.

The full (unretarded) zero-order rates of hydrochlorination of natural rubber latex are reproduced with synthetic polyisoprene (to about 8% accuracy) in the two runs at 300° K and at 2 atm. of HCl, and the one run of four points taken at the same temperature and 1 atm. of HCl (Table ; Figs. 2 and 3). The decrease in rate between the two pressures is given by a factor of 9·1 within experimental error with both substrates.

The zero-order kinetic law may be explained *a priori* by either of two opposing hypotheses : (i) The rate-determining step involves the polymer, but the disappearance of the polymer units due to hydrochlorination leaves the rate unaffected for special reasons of compensation, such as might arise in a chain-reaction mechanism. (ii) The rate-controlling step involves only species derived from hydrogen chloride, and possibly water, whose concentrations are maintained constant during each run in the surrounding aqueous phase.

Since stereochemical considerations lead to the postulate (*idem, ibid.*) of a chain reaction for the hydrochlorination of natural latex, we need to discuss (i) in some detail. The discussion will show that this hypothesis is hardly tenable, since any zero-order rate obtained will be sensitive to the number or kinetic length of the chains involved, which in turn will be sensitive to the detailed structure of the polymer and could hardly survive unchanged a change of substrate from rubber to polyisoprene. Zero-order laws can arise in the following two fundamental types of chain mechanisms :

(1*a*) *Life-time of reaction chain comparable with total reaction time.* A long linear portion of the rate curve, followed by a rounded portion leading to asymptotic decay, may be observed. A relevant plot is given by Jellinek (*J. Polymer Sci.*, 1952, **9**, 369, Fig. 2) in connection with certain degradation mechanisms of vinyl polymers, and such a plot could readily be fitted to our results on the main hydrochlorination of rubber and polyisoprene. The straight-line portion must then be the result of a constant number of reaction chains, started simultaneously at the beginning of the reaction, and propagated with constant average rate. The initiation must be at chemically privileged units of the polymer, and the propagation must pass along the polymer chain. The privileged units must be very evenly spaced, to ensure a constant length of polymer, and thus a constant kinetic chain length, between them. (In particular, since the polymer chains in rubber are far from constant in length, the privileged units for activation cannot merely be end units.) The kinetic chain length must be about thirty units or more. If these conditions do not apply, the linear portion of the rate curve will be much shorter than was observed. (Of course the rounded portion at the end is due to the fact that the chains, though initiated simultaneously and of even chain-length, will not die simultaneously. Their life-time would be governed by a Poisson-type distribution, because propagation is subject to the hazard of random encounters.) While we earlier entertained the theory that a small number of evenly spaced, chemically active, initiating groups might be present in natural rubber, the same number and spacing of such groups cannot also be characteristic of the synthetic polymer, so that mechanism (1*a*) has to be abandoned.

(1*b*) *Life-time of reaction chain small with respect to total reaction time.* The following equation would apply :

$$\text{Overall rate} = \text{Initiation rate} \times \text{Kinetic chain length}$$

By constancy of the two factors on the right (as in certain photochemical experiments), or by their reciprocal variation, a linear rate law may be achieved. Both factors would again depend critically on the detailed structure of the polymer units, so that it is again impossible to understand how the same constant rate could be obtained for the natural and the synthetic polymer. It is thus clear that the presence of a chain reaction magnifies the sensitivity of what is always the most searching test for non-participation of the substrate in the rate-control, *viz.*, an actual change in substrate. An example of the application of this test from the field of reactions of inorganic acids with organic substrates is found in the zero-order nitration, explained by Hughes, Ingold, and Reed (*J.*, 1950, 2410) as controlled by the rate of the reaction $O_2N{\cdot}OH \longrightarrow O_2N^+ + OH^-$.

Next, having rejected the possible schemes (1*a* and *b*) for intervention of the substrate, we require to seek, in accordance with hypothesis (ii) above, for a rate-determining step involving only the hydrochloric acid (and possibly water) for the hydrochlorination of our two substrates.

Nature of the Rate-controlling Step.—The rate of this step will follow the fundamental Brønsted equation :

$$\text{Rate} = ka_1^m a_2^n \ldots . /f_T \qquad (2)$$

where the *a*'s are the activities of the colliding species and f_T is the activity coefficient of the transition state. The reaction takes place in the hydrocarbon phase and probably between ions, as will be shown. It thus falls into a class of reactions for which there is little knowledge to draw on. A concrete suggestion as to the nature of the step emerges from the temperature and concentration effects so far measured, but full proofs remain the subject of further study.

The partial pressures of water (almost negligible) and hydrogen chloride being constant for each kinetic run, the activities of all species which are in equilibrum with these vapours will likewise remain constant. The rate-controlling step must produce a highly *reactive species* (cf. NO_2^+ for nitration), immediately taken up by the rubber substrate, from certain *precursors* (cf. $O_2N{\cdot}OH$ for nitration). The precursors are here in diffusive equilibrium with the aqueous and hence with the vapour phase, as otherwise the *a*'s in equation 2 would vary and zero-order rate plots would not be obtained over wide ranges of temperature and acid pressure. If the precursors can be maintained in diffusive equilibrium across the rubber-particle surface, the same must be true of neutral, covalent hydrogen chloride molecules, which are the stable dissolved species of the acid in hydrocarbon media. This is confirmed by the finding (Wynne Jones, *J.*, 1930, 1064) that the small amount of hydrogen chloride dissolved in benzene (saturated with water) at 25° follows Henry's linear law of pressure *versus* mole fraction. The slope of the line, incidentally, lies well below 50% of that for Raoult's law, thus showing that the solution is not a completely ideal one. If hydrogen chloride molecules are in diffusive equilibrium with the aqueous phase, they cannot constitute the reactive species formed in the rate-determining step, whose equilibrium must be completely upset by the fast reaction with rubber. If the reactive species were in diffusive epuilibrium with the aqueous phase, the rate of latex hydrochlorination (g. of HCl per c.c. of latex per sec.) would be independent of the rubber concentration, instead of proportional to it (*i.e.*, the rubber would behave like a dissolved species in the zero-order reaction, not like a separate phase).

Another important conclusion follows from the constancy of the rate between about 20 and 80% hydrochlorination. According to equation (2), f_T as well as the a's must be constant, and this despite the considerable change in the reaction medium (particularly the dielectric constant) occurring as rubber is progressively converted into its hydrochloride. This constancy of f_T must mean that there is no net charge on the transition state which converts the precursors into the reactive species.

The unknown true activation energy of hydrochlorination may be expected to be considerable (say, >15 kcal.), since a H–Cl bond has to be broken and a C=C converted into a C–C bond. The apparent energy of activation at constant activity (pressure) of hydrogen chloride is an appreciably negative quantity, −6 kcal. on an average for natural rubber at 1 atm. between 0° and 27°. Such a decrease in rate with rising temperature is generally to be explained as due to a pre-equilibrium, producing reaction precursors exothermally, and thus (by le Chatelier's principle) reducing their activities in equation (2) with rising temperature. It is not likely that the pre-equilibrium, with an exothermic forward reaction, which concerns us is merely the dissolution of hydrogen chloride gas in the polymer particles, as the heat of dissolution can hardly be large enough to depress the apparent activitation energy so markedly. If hydrogen chloride were an ideal solute in rubber, we should equate this heat of solution to its heat of condensation (into pure liquid HCl), *viz.*, about 3·5 kcal. Even if the true value were twice as great, and two separate HCl molecules were required as precursors, the resulting depression of the activation energy, $2 \times 2 \times 3{\cdot}5 = 14$ kcal., falls well below the expected range. It is thus likely that the effect of a chemical equilibrium is superimposed on the dissolution equilibrium, thus subtracting a further substantial heat of reaction from the heat of formation of the actual precursors in the polymer phase, and thus adding it to the activation energy. This suggests that the precursors are ionic, for un-ionized derivatives of hydrogen chloride would hardly be substantially exothermic. The heat liberated in the formation of ions may be called " heat of solvation," but little is known about the nature of ion solvation in wet hydrocarbon media.

The various strands of evidence combine to suggest that the rate-controlling step is the formation of an uncharged, but not covalent, form of hydrogen chloride from ionic precursors. This means that a neutralization step creates an " ion pair " as the reactive species which combines with the rubber. Disregarding solvation, we write this :

$$H^+ + Cl^- \longrightarrow (H^+, Cl^-) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

In water, H^+ is known to be solvated as H_3O^+, but the high dependence of the isothermal rate of hydrochlorination of rubbers on hydrogen chloride pressure favours the assumption that H_2Cl^+ is concerned as the positively charged precursor in the rubber phase. (The concentration of H_2Cl^+ will be governed by an acidity function H_0. We hope to discuss this later, as acidity-function measurements are being extended to our concentration range in this College at present.) Reaction (3) may thus prove to be more correctly written :

$$H_2Cl^+ + Cl^- \longrightarrow (H^+, Cl^-) + H\text{–}Cl \quad . \; . \; . \; . \; . \; . \quad (4)$$

The right-hand side of (4), as regards the formation of a reactive ion pair, is more certainly indicated by our present kinetic evidence than the precise nature of the precursors on the left. Since the main barrier in the overall addition of gaseous hydrogen chloride to rubber must be the breaking of the H–Cl bond, and since ion pairs are familiar species in media of low dielectric constant, the reactive species proposed may be accepted with considerable confidence : it presents the rubber with the elements of hydrochloric acid, but with the covalency broken. Fig. 4 sketches qualitatively the possible energy levels for the early steps in the hydrochlorination reaction, up to the reactive ion pair (which converts an isoprene unit into its hydrochloride very quickly). This sketch brings out the fact that the observed activation energy E is negative and constant, leading to a constant rate independent of reaction progress at each temperature, while the true activation energy ΔH^* is positive and may vary with the reaction progress. Although the energy level of the ionic precursors should drop as the dielectric constant of the polymer increases owing to the hydrochlorination progress, the level of the transition state T, which bears no net charge, remains unaffected. It is to this fortunate circumstance that we owe any understanding of this complicated reaction. Fig. 4 implies that the formation of rubber hydrochloride from gaseous hydrogen chloride and rubber must be exothermic to at least the extent of the observed energy of activation (6 kcal.), since the energy level of rubber hydrochloride must lie below that of the transition state T. According to reaction (4), this state will not differ greatly from two hydrogen chloride molecules in collision, which agrees well with its observed energy level 6 kcal. below the gas, since this represents closely the level of two hydrogen chloride molecules regarded as an ideal solute (about 7 kcal. below the gas).

In the aqueous phase ion pairs might well be formed very much more rapidly than in the polymer, thus accounting for the fast initial surface reaction. For the chain reaction proposed on stereochemical grounds for the latex hydrochlorination of natural rubber (Gordon and Taylcr, *J. Appl. Chem.*, in the press), it has been pointed out that the hydrogen chloride must react in a form bearing no net charge with the chain-carrying rubber units, in order to leave their charge-type unchanged. The deduction of an ion pair as the reactive species, based in particular on the constancy of f_T with reaction progress, is a welcome confirmation of this. However, according to the nature of the rate control revealed in this paper, no other contact between Gordon and Taylor's stereochemical theory and the kinetic data obtained to date can emerge; since the rate-controlling step (4) is merely a preliminary to the attack on the rubber, the kinetics are equally compatible with reaction chains passing along the polymer molecules, and with non-chain (random) mechanisms. If the specific chain mechanism proposed by Gordon and Taylor for natural rubber is correct, very different reaction steps are likely to succeed the controlling step (4) in rubber and in synthetic polyisoprene, because of the structural differences mentioned earlier. All succeeding steps must, in the light of the observed kinetics, occur rapidly with respect to the life-time of the reactive ion pair.

Total Attainable Conversion.—In the past, the hydrochlorination reaction of natural and synthetic rubber has always fallen short of stoicheiometric conversion, when judged by the chlorine content of the final product. This is of technical importance, because the unchanged double bonds in rubber hydrochloride constitute a source of weakness, *e.g.*, in the ageing characteristics of packaging films. Van Veersen (*loc. cit.*) obtained higher conversions (up to 98·7 mole %) from his natural-latex process than is obtainable in solution (usually not more than 90%). The same is evidently true, to an even greater extent, for synthetic polyisoprene, since we readily obtain 99·5% conversion with our latices, which is within experimental error of complete conversion. D'Ianni (*loc. cit.*), working with this substrate in solution, did not obtain more than 83% hydrochlorination and ascribed this to the unreactive nature of vinyl groups resulting from 1 : 2-addition. The high conversion we register with our latices, despite the variable nature of the isoprenic groups present, shows that they all react readily with the reactive form of HCl (interpreted as an ion pair) formed in the latex process. Moreover, it confirms that the incomplete hydrochlorination obtained in other processes with various rubbers is not attributable to thermodynamic reversibility of the reaction. Our results to date are consistent with the explanation of the premature arrest of the natural latex hydrochlorination in terms of increasingly difficult diffusion of hydrogen chloride through the large and increasingly crystalline particle.

We thank Professor P. D. Ritchie for his interest and encouragement, and Mr. J. W. Sharpe for his work with the electron-microscope, which will be published separately. One of us (J. S. T.) thanks the D.S.I.R. for a maintenance allowance.

DEPARTMENT OF TECHNICAL CHEMISTRY, ROYAL TECHNICAL COLLEGE,
GLASGOW, C.1.

[*Received, July 6th*, 1953.]